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by

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## ABSTRACT

Strict ambient air quality standards for  $\text{SO}_2$  and  $\text{NO}_x$  in Japan mandate the use of various air pollution control technologies. This report is a compilation of information on the current status of  $\text{NO}_x$  abatement technologies for stationary sources in Japan. The author obtained this information from electric power companies, various industries, and developers of numerous technology processes, as well as from his own original research in the field. The report focuses on the combustion modification (CM) and Selective Catalytic Reduction (SCR)  $\text{NO}_x$  abatement technologies. Information is provided on the development status, pilot and demonstration plant tests, technological problems, and costs associated with the use of these technologies in Japan. Detailed operation data is given to describe the commercial operation of SCR plants.

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## SUMMARY

### NO<sub>x</sub> Standards and Ambient Concentrations

Recent air pollution control efforts in Japan have concentrated on NO<sub>x</sub> abatement, since ambient SO<sub>2</sub> concentrations already have been drastically reduced in response to stringent standards. In 1978, the ambient air quality standard for NO<sub>2</sub> was amended from 0.02 ppm to the range of 0.04 to 0.06 ppm as a daily average. In regions with NO<sub>2</sub> concentrations above 0.06 ppm, the concentration will be reduced to 0.06 ppm by 1985. In regions where NO<sub>2</sub> concentrations range from 0.04 to 0.06 ppm, efforts will be made to keep the concentrations from substantially exceeding the present level. In areas where the concentration falls below 0.04, efforts must be made to keep at that level. The new NO<sub>2</sub> standard is relaxed compared with the previous standard, 0.02 ppm as a daily average, but is still more stringent than the U.S. standard of 0.05 ppm as a yearly average.

In regions with large cities such as Tokyo and Osaka, ambient NO<sub>2</sub> concentrations often exceed the standards, reaching 0.07-0.08 ppm as daily averages. The prefectural governments of Chiba, Kanagawa, and Mie have established even more stringent regulations and plan to reduce NO<sub>2</sub> concentrations to 0.04 ppm from the current 0.05-0.06 ppm level. Even in regions with NO<sub>2</sub> concentrations below 0.04 ppm, NO<sub>x</sub> reduction is often required by local governments to prevent any further increase.

Nearly 2 million tons/year of NO<sub>x</sub> is emitted in Japan, 60% of which is derived from stationary sources and the rest from mobile sources. In large cities such as Tokyo and Osaka, about 60% of the NO<sub>x</sub> is emitted from mobile sources.

NO<sub>x</sub> emissions from gasoline engine passenger cars manufactured since 1978 have been controlled by stringent regulations. The current limit is 0.25 gram/km, which amounts to 8% of the NO<sub>x</sub> emissions from cars in 1973. NO<sub>x</sub> emissions from diesel-engined buses and trucks have been reduced to about 50% of the 1974 level. For stationary combustion sources, emission standards based on advanced combustion modification technology has been applied to reduce NO<sub>x</sub> by 30-70%.

With these efforts, ambient NO<sub>2</sub> concentrations are no longer increasing despite a continuing increase in the number of stationary and mobile sources. However, it is difficult to lower current NO<sub>2</sub> concentrations in large cities and industrial regions without more effective emission controls for diesel engine cars and stationary sources.

#### NO<sub>x</sub> Reduction for Stationary Sources

Nearly all NO<sub>x</sub> emissions are produced by the combustion of fossil fuels. In Japan, the major combustion fuel is heavy oil. This residue of the atmospheric distillation of crude oil has been used at the rate of nearly 200 million kiloliters per year. Coal use decreased markedly between 1965 and 1975 and currently accounts for only 3% of the nation's total energy supply. However, coal consumption is expected to triple in the next 10 years. Imported LNG also accounts for about 3% of the energy currently used and is expected to nearly triple in 10 years.

Large stationary sources such as utility boilers have reduced NO<sub>x</sub> emissions 50-70% by applying combustion modifications (CM) including low excess air combustion, staged combustion, flue gas recirculation and low-NO<sub>x</sub> burners. As a result, the NO<sub>x</sub> concentration in flue gas from utility boilers is minimal---150-300 ppm for coal, 80-120 ppm for oil, and 40-60 ppm for gas firing. Smaller boilers and furnaces have reduced NO<sub>x</sub> 30-50% by using low-NO<sub>x</sub> burners or by switching from heavy oil to kerosene fuel.

For additional NO<sub>x</sub> abatement, several flue gas treatment (FGT) processes have been developed. Of all the processes, selective catalytic



reduction (SCR) which uses ammonia and a catalyst at 300-400°C to control  $\text{NO}_x$ , is presently the most advanced technology. Over 150 commercial SCR plants are in operation to remove 80-90% of the  $\text{NO}_x$  emissions. Selective noncatalytic reduction (SNR) which uses ammonia at 800-1,000°C to remove 30-50% of  $\text{NO}_x$  emissions has been developed and applied to about 20 furnaces and industrial boilers. Wet and dry simultaneous  $\text{SO}_x$  and  $\text{NO}_x$  removal processes also have been developed but have not been applied commercially except for several small units.

SCR has been used most often for flue gas treatment because of its simplicity (which enables unattended operation), relatively high  $\text{NO}_x$  removal efficiency (80-90%), and relatively low cost. Most of the new coal-fired utility boilers being planned will have SCR units. SCR will also be needed for some of the existing boilers even in regions with  $\text{NO}_x$  concentrations below a 0.04 ppm daily average, due to local policies which forbid any increase in  $\text{NO}_x$  levels. For example, when a new boiler is installed at a power station, not only the new boiler, but also some of the existing boilers will be required to have SCR units so that total  $\text{NO}_x$  emissions from the station do not increase.

SCR is usually used with CM. For most boilers and furnaces, CM is applied first, followed by SCR in order to meet the stringent regulations. For over 90%  $\text{NO}_x$  reduction, the combination of CM (to reduce 35-50% of the  $\text{NO}_x$  emissions) and SCR (to remove 80-85% of the remaining  $\text{NO}_x$ ) is usually more economical than SCR by itself.

Typical examples of uncontrolled and controlled  $\text{NO}_x$  concentrations in utility boiler flue gas are shown in Table S-1. Examples of  $\text{NO}_x$  regulations and emissions from utility boilers are shown in Table S-2.

A new combustion process, in-furnace  $\text{NO}_x$  removal, has been developed to remove about 50% of  $\text{NO}_x$  by injecting a small portion of the fuel above the flame, followed by air addition to assure complete combustion. By using this process along with CM for utility boilers,  $\text{NO}_x$  may be reduced to 100 ppm for coal, 50 ppm for oil, and 20 ppm for gas.



TABLE S-1. EXAMPLES OF CONTROLLED AND UNCONTROLLED NO<sub>x</sub> CONCENTRATIONS IN UTILITY BOILER FLUE GAS

| Fuel | Without Control, ppm | Outlet NO <sub>x</sub> Concentration (ppm) |                          | Percent Control |        | TOTAL % CONTROL |
|------|----------------------|--------------------------------------------|--------------------------|-----------------|--------|-----------------|
|      |                      | Controlled By CM                           | Controlled By CM and SCR | by CM           | by SCR |                 |
| Gas  | 200                  | 50                                         | 10                       | 70              | 83     | 95              |
| Oil  | 300                  | 100                                        | 20                       | 67              | 80     | 93              |
| Coal | 600                  | 250                                        | 50                       | 58              | 80     | 91              |

TABLE S-2. EXAMPLES OF NO<sub>x</sub> REGULATIONS AND EMISSIONS FROM UTILITY BOILERS (ppm)

| Fuel | Boiler   | Central Government | Local Agreement  | Actual Emission  |
|------|----------|--------------------|------------------|------------------|
| Gas  | Existing | 100                | 60               | 60 <sup>a</sup>  |
| Gas  | New      | 60                 | 10               | 8 <sup>b</sup>   |
| Oil  | Existing | 150                | 100              | 100 <sup>a</sup> |
| Oil  | New      | 130                | 25               | 20 <sup>b</sup>  |
| Coal | Existing | 400                | 159 <sup>d</sup> | 170 <sup>a</sup> |
| Coal | New      | 400                | 170              | 160 <sup>c</sup> |

<sup>a</sup>By combustion modification (CM).

<sup>b</sup>By CM and selective catalytic reduction (SCR).

<sup>c</sup>By CM and partial SCR.

<sup>d</sup>Desired by local government.

Fluidized bed combustion, gasification, and liquefaction of coal all have been tested in Japan, but these technologies are not as advanced there as they are in the U.S. This is because Japan must import coal and because these technologies are unable to meet the stringent Japanese  $\text{NO}_x$  emission regulations. Most of the new coal-fired boilers in Japan will use conventional pulverized coal combustion with CM, SCR and FGD.

#### SCR and SCR/FGD Characteristics

In the past SCR has experienced several problems, but these have been solved by recent improvements. The major problems were: 1) poisoning of the catalyst by  $\text{SO}_x$  in the gas, 2) dust plugging of the catalyst, and 3) deposition of ammonium bisulfate in the air preheater downstream of the SCR reactor. Catalyst poisoning has been eliminated by using catalysts based on  $\text{TiO}_2$  instead of  $\text{Al}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3$ . The use of parallel-flow honeycomb, tube or plate catalysts or a parallel passage reactor eliminates dust plugging. Ammonium deposits can be prevented by maintaining the concentration of unreacted ammonia in the reactor outlet gas below 5 ppm and using a low-oxidation catalyst. To do this, 0.82-0.95 mole  $\text{NH}_3$  is usually used per mole  $\text{NO}_x$  to obtain 80-90%  $\text{NO}_x$  removal with less than 5 ppm unreacted  $\text{NH}_3$ , while  $\text{SO}_2$  oxidation is kept below 1%.

SCR and FGD system applications to boilers and other gas sources are schematically shown in Figure S-1. SCR is easily applied to boiler economizer outlet gas at 300-400°C as shown in the A portion of the figure. For  $\text{SO}_x$ -rich gases, FGD may be applied downstream of SCR as shown in B. At an early stage of development, SCR was applied downstream of FGD systems, as shown in C, to protect the catalyst from  $\text{SO}_x$  attack. System C, however, is expensive since it requires large amounts of energy for gas reheating. System B has become popular as  $\text{SO}_x$ -resistant catalysts have been developed.

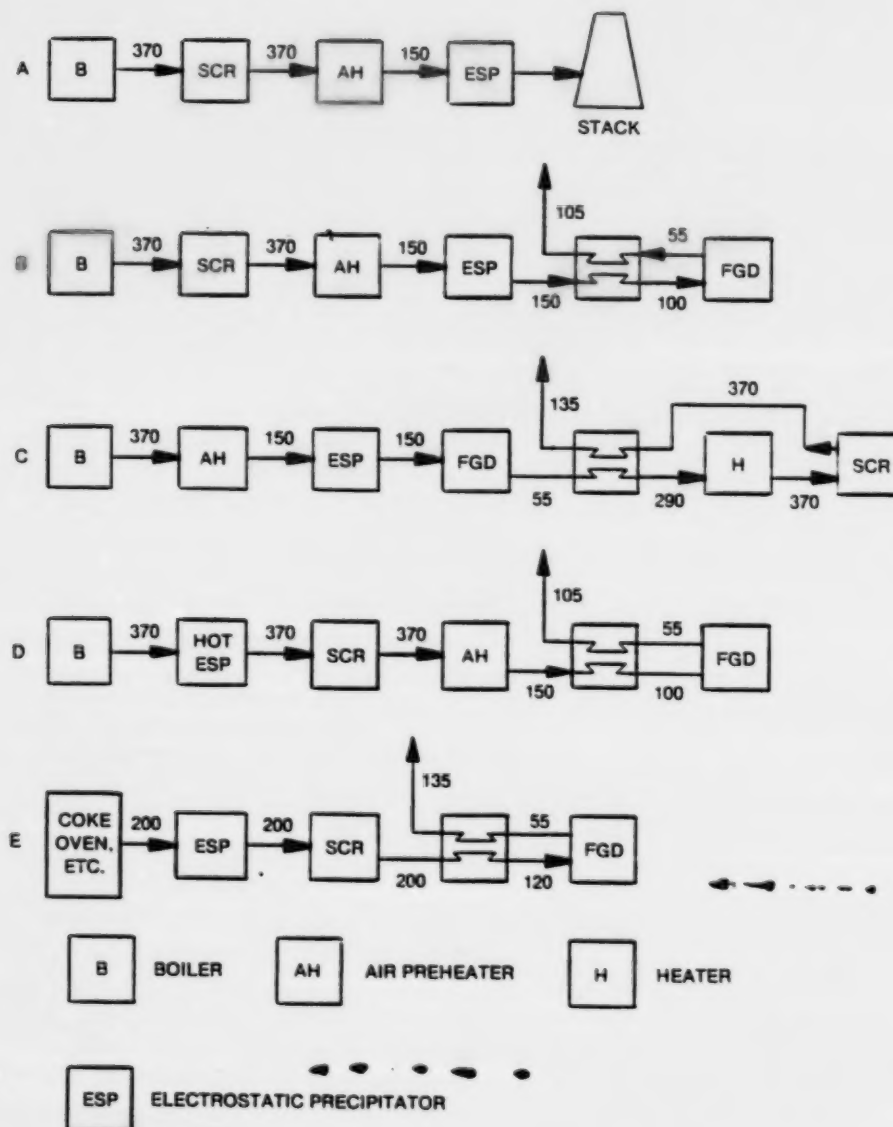


Figure S-1 SCR and FGD System Arrangements in Use in Japan.  
(numbers indicate gas temperature in °C)

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System D is often used for flue gas from a low-sulfur coal. In this system, the boiler economizer outlet gas is first treated by a hot electrostatic precipitator (ESP) and then by SCR and FGD. A cold ESP is not highly efficient for flue gas from low-sulfur coal. For high-and medium-sulfur coals, system B is preferable. System B may also be useful for low-sulfur coal provided that both the cold ESP and the FGD unit are designed for sufficient dust removal.

Low-temperature catalysts have been used for 200-250°C gases such as that produced by coke ovens, as shown in system E of Figure S-1. Since ammonium bisulfate deposits on the catalyst at these low-temperatures, the catalyst requires occasional heating to 400°C to remove the bisulfate.

When wet FGD is applied downstream of SCR or SNR, the ammonia present in the reactor outlet is caught by the FGD system and goes into the wastewater. In some cases it may be necessary to use the activated sludge process to remove ammonia from the wastewater.

#### Cost of NO<sub>x</sub> Abatement for Stationary Sources

The investment cost for a combustion modification system is shown in Table S-3. Costs range from ¥400 to 800 per Nm<sup>3</sup> of flue gas or ¥1,200-2,400/kW for 55-70% reduction using a combined low-NO<sub>x</sub> burner, staged combustion, and flue-gas recirculation system.

TABLE S-3. CM INVESTMENT COST

| Method                       | NO <sub>x</sub> removal (%) | Yen/Nm <sup>3</sup> | Yen/Kw    | \$/Kw <sup>a</sup> |
|------------------------------|-----------------------------|---------------------|-----------|--------------------|
| Low-NO <sub>x</sub> burner   | 20-40                       | 100-200             | 300-600   | 1.2-2.4            |
| Combined System <sup>b</sup> | 50-70                       | 400-800             | 1200-2400 | 4.8-9.6            |

<sup>a</sup>\$1 = ¥ 250

<sup>b</sup>Low-NO<sub>x</sub> burner, staged combustion and flue gas recirculation

SCR costs for new 700 MW gas-, oil-, and coal-fired utility boilers are shown in Table S-4. For cost estimation purposes, it was assumed that flue gases leaving the boiler economizer at 330-400°C are treated in two equal size reactors in parallel and that unreacted  $\text{NH}_3$  is kept below 5 ppm. The investment cost for 80%  $\text{NO}_x$  removal is about ¥2,500/kW for gas, ¥4,100-6,200/kW for oil, and ¥6,700-8,400/kW for coal. The cost differences are due to the varying amounts of catalyst required. For example, a small amount of a very active catalyst is used for gas streams while a larger amount of a less active catalyst which is resistant to  $\text{SO}_x$  and dust erosion is used for dirty flue gas (oil or coal streams). Compared with 80% removal, 90% removal costs 15% more for gas, 25-30% more for oil, and 30% more for coal. The investment cost of an SCR system for an existing boiler is 10-50% more than for a new boiler.

The dirtier the gas, the shorter the life of the catalyst. Therefore, the annualized SCR cost/kWhr is higher when SCR is used with dirty gas. On the other hand, the annualized cost per pound of  $\text{NO}_x$  removed is lower with  $\text{NO}_x$  rich gas. The cost per pound for 80% removal is 10-17 percent lower than the cost for 90% removal. Ninety percent  $\text{NO}_x$  removal with a low level of unreacted  $\text{NH}_3$  (about 5 ppm) is not easy to obtain with a large amount of gas from a utility boiler. The reason for this is that both gas velocity and  $\text{NO}_x$  concentrations vary across the duct at the reactor inlet.

The investment and annualized SCR costs for 80%  $\text{SO}_2$  removal for coal-fired boilers are about one-third of those for 90%  $\text{SO}_2$  removal using the wet lime/limestone FGD process. On the other hand, SCR is more expensive than CM. Although the investment cost of SCR for a gas-fired boiler is similar to that of CM in the combined system (Table S-3), the annualized cost of SCR may be considerably higher than CM, which has low operating costs. Therefore, for  $\text{NO}_x$  abatement, CM should be used first and SCR should be used in combination with CM when CM alone is not sufficient to meet control regulations. One CM technique, flue gas recirculation, is relatively expensive and is not highly efficient for coal. For this reason, flue gas recirculation may not be useful when SCR is applied to coal-fired boilers.



TABLE 8-4. SCR COST FOR 700 MW NEW BOILER (1981 COST)  
(70% BOILER UTILIZATION 4,292,000 kWhr/year)

| Fuel                                           | Gas    | Low-S<br>Oil | High-S<br>Oil | Low-S<br>Coal | High-S<br>Coal | High-S<br>Coal |
|------------------------------------------------|--------|--------------|---------------|---------------|----------------|----------------|
| Inlet NO <sub>x</sub> ppm                      | 60     | 100          | 200           | 300           | 300            | 600            |
| Catalyst<br>Type                               | pellet | Honeycomb    | Honeycomb     | Honeycomb     | Honeycomb      | Honeycomb      |
| Cost, 10 <sup>4</sup> yen/m <sup>3</sup>       | 3.0    | 3.3          | 3.3           | 3.5           | 3.5            | 3.5            |
| Life, year                                     | 4      | 3            | 3             | 2             | 2              | 2              |
| NO <sub>x</sub> removal, percent               | 80     | 90           | 80            | 90            | 80             | 90             |
| Investment Cost <sup>a</sup><br>(1,000 yen/kW) | 2.47   | 2.80         | 4.13          | 5.11          | 6.23           | 7.93           |
| Annualized cost <sup>b</sup><br>(yen/kWhr)     | 0.17   | 0.20         | 0.28          | 0.35          | 0.44           | 0.56           |
|                                                |        |              |               | 0.59          | 0.76           | 0.81           |
|                                                |        |              |               |               | 0.82           | 1.04           |

<sup>a</sup>Including initial charge of catalyst, civil engineering, and test operation.

<sup>b</sup>Including 10% interest and 7 years depreciation

The costs of other FGT processes are uncertain because they have not been used widely in continuous commercial operation. However, experience with Thermal DeNO<sub>x</sub>, a type of SNR used with an oil-fired utility boiler, indicates that its cost is about half that of SCR although the NO<sub>x</sub> removal efficiency is also half as much (40% versus 80%).

## SECTION 1

### NO<sub>x</sub> EMISSIONS AND CONTROL

#### 1.1 ENERGY AND NO<sub>x</sub> EMISSIONS

Between 1960 and 1973 the energy supply in Japan increased sharply and then dropped slightly during the 1974 oil crisis. Since 1975 the energy supply has been increasing steadily (Figure 1-1). In 1980, 66.4% of Japan's total primary energy supply was dependent on imported oil (Table 1-1). The Japanese government intends to restrict oil imports to 366 million kiloliters after 1985, and to increase the use of other fuels, mainly atomic power and coal. By 1990, 50% of the nation's total energy supply will come from sources other than imported oil.

Japan's supply of domestic coal cannot exceed 20 million tons annually because of its deep and small native mines; this necessitates the importation of coal. In 1980, imported coal exceeded 70 million tons; nearly all of it was used for coke production in the steel industry. Imported coal for fuel is expected to increase rapidly in the next few years, reaching 22 million tons in 1985, and 53 million tons in 1990.

Man-made NO<sub>x</sub> emissions in Japan total about 2 million tons annually. About 60% of the total emissions are derived from stationary sources and the rest from mobile sources; in large cities, as much as 50-60% of the NO<sub>x</sub> comes from mobile sources.

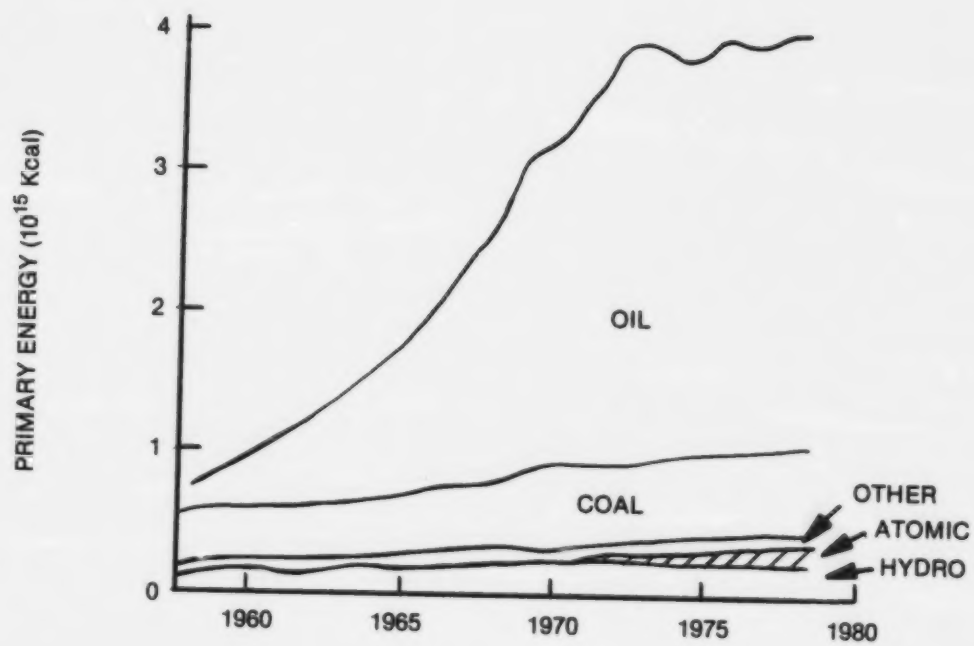


Figure 1-1 Primary Energy Supply in Japan: 1960 - 1980.

TABLE 1-1. JAPAN'S ENERGY SUPPLY: 1980-2000 (MITI, 1982)

|                                                      | 1980   |        | 1990    |        | 2000   |        |
|------------------------------------------------------|--------|--------|---------|--------|--------|--------|
|                                                      | Amount | (%)    | Amount  | (%)    | Amount | (%)    |
| Coal, total (10 <sup>6</sup> t)                      | 92.4   | (16.7) | 153     | (19.5) | 200    | (19.0) |
| Domestic                                             | 18.1   |        | 18~20   |        |        |        |
| Imported                                             | 74.3   |        | 133~135 |        |        |        |
| For Power Generation                                 | 21.3   |        | 66      |        |        |        |
| Atomic Power (10 <sup>6</sup> kW)                    | 15.7   | (5.0)  | 46      | (11.3) | 90     | (18.0) |
| Natural Gas, total (10 <sup>6</sup> kl) <sup>a</sup> | 25.9   | (6.0)  | 68      | (11.5) | 82     | (11.0) |
| Domestic (10 <sup>6</sup> m <sup>3</sup> )           | 2.2    |        | 7.3     |        |        |        |
| LNG (10 <sup>6</sup> t)                              | 16.8   |        | 43      |        |        |        |
| Hydro Power (10 <sup>6</sup> kW)                     | 29.8   | (5.6)  | 45.5    | (5.0)  | 63     | (5.0)  |
| Geothermal (10 <sup>6</sup> kl) <sup>a</sup>         | 0.3    | (0.1)  | 6       | (1.0)  | 15     | (2.0)  |
| New Energy, etc. (10 <sup>6</sup> kl) <sup>b</sup>   | 0.7    | (0.2)  | 15      | (2.5)  | 65     | (8.0)  |
| Oil, total (10 <sup>6</sup> kl)                      | 286.6  | (66.4) | 290     | (49.2) | 290    | (37.0) |
| Domestic                                             | 0.5    |        | 1.9     |        |        |        |
| TOTAL (10 <sup>6</sup> kl)                           | 429    | (100)  | 590     | (100)  | 770    | (100)  |

<sup>a</sup>Counted as oil energy<sup>b</sup>Including solar energy, coal gasification, charcoal, etc.



Figure 1-2 shows annual  $\text{NO}_x$  emissions from large stationary sources. The emissions from utility boilers add up to about 310,000 tons which account for 34% of the emissions from large sources. As larger amounts of coal are used the emissions from utilities may increase significantly (Figure 1-3). Although extensive efforts have been made to reduce  $\text{NO}_x$  from both mobile and stationary sources, further  $\text{NO}_x$  abatement efforts will be needed for future coal-fired boilers.

New coal usage techniques, fluidized-bed combustion (FBC), and coal gasification and liquefaction have been tested by many Japanese organizations. Figure 1-4 shows the Japanese Government's 1978 preliminary plan for development of coal gasification and liquefaction. Called the Sunshine Project, this work is being carried out in cooperation with various industries under the leadership of the Japanese government. In addition, private companies have been trying to develop these technologies by themselves or through international cooperation.

Development of FBC and coal liquefaction and gasification is not as advanced in Japan as it is in the U.S. Japan is handicapped by the necessity of importing coal and by stringent  $\text{NO}_x$  emission regulations. These regulations often require  $\text{NO}_x$  removal from the exit flue gases of FBC or coal gasification and liquefaction systems. In addition, each process has the following disadvantages.

**FBC:** Japan has no land available for disposal of the process' throwaway ash containing lime and calcium sulfate. Although the absorbent may be regenerated and recycled, this approach may be too costly.

**Gasification:** For utility boilers, conventional pulverized coal combustion with flue gas treatment by SCR of  $\text{NO}_x$ , ESP, and FGD may be less costly and more reliable than gasification with combined cycle power generation; both FGD and SCR have proved to be highly reliable in Japan. For industry, there has been little need to use gas produced from coal. Japan plans to import increasing amounts of LNG, a large portion of which will be burned at power

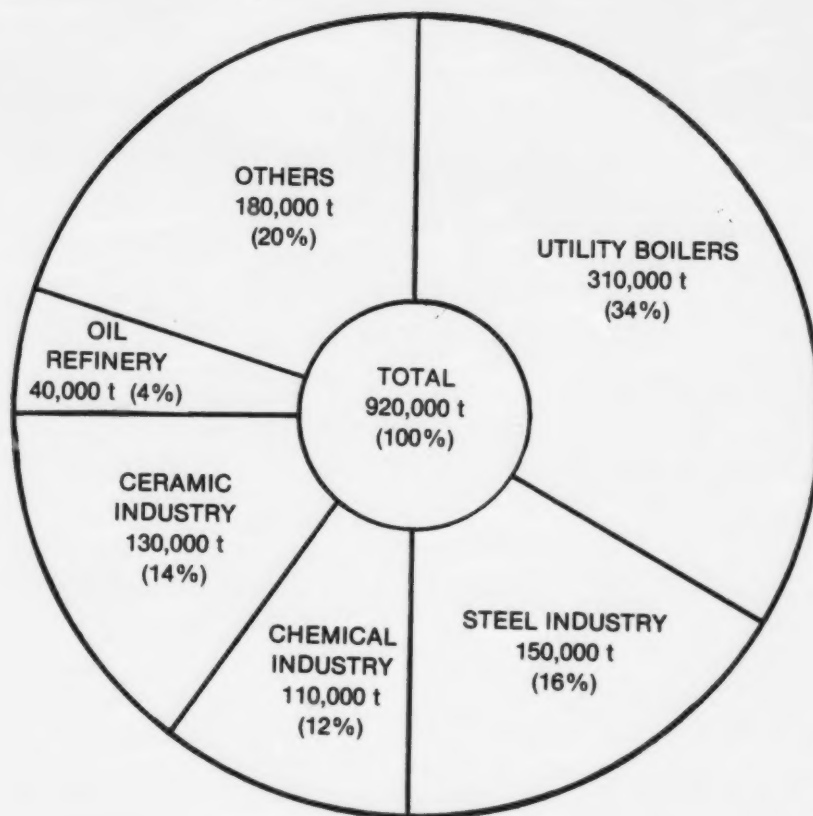


**Figure 1-2 Annual NO<sub>x</sub> Emissions from Stationary Sources.**

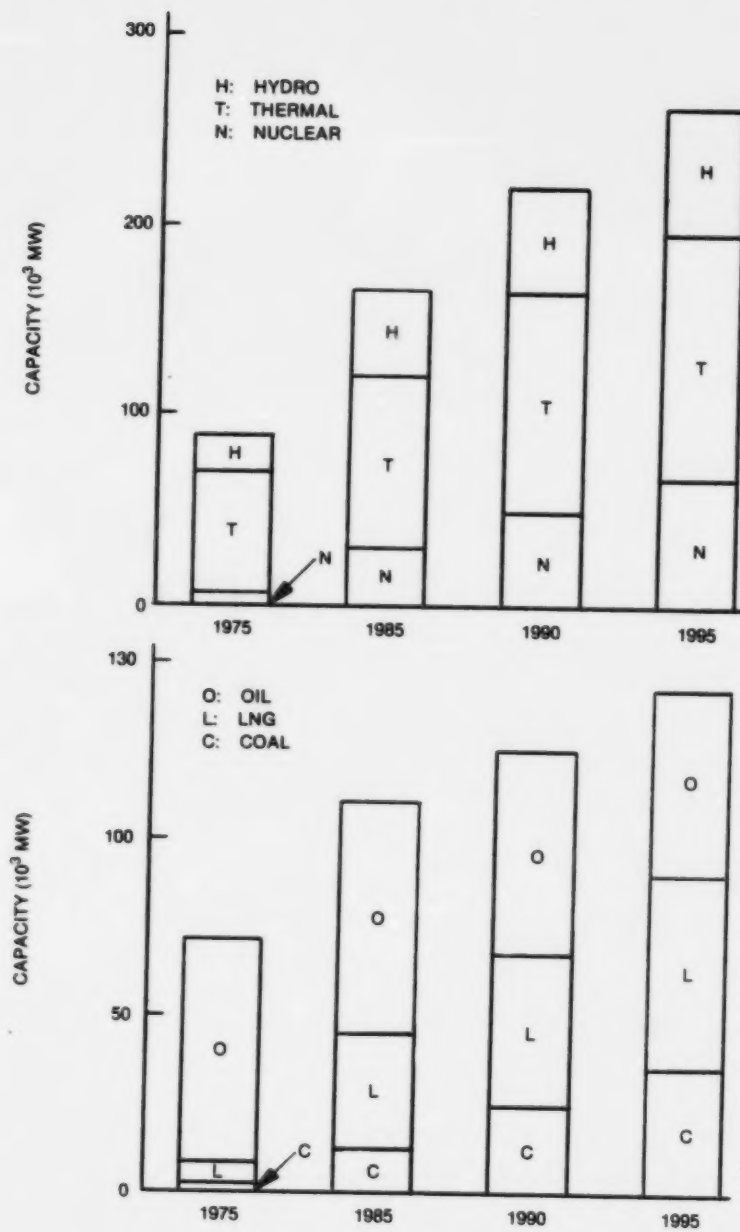


Figure 1-3 Estimated Increase in Electrical Power Generation Capacity.

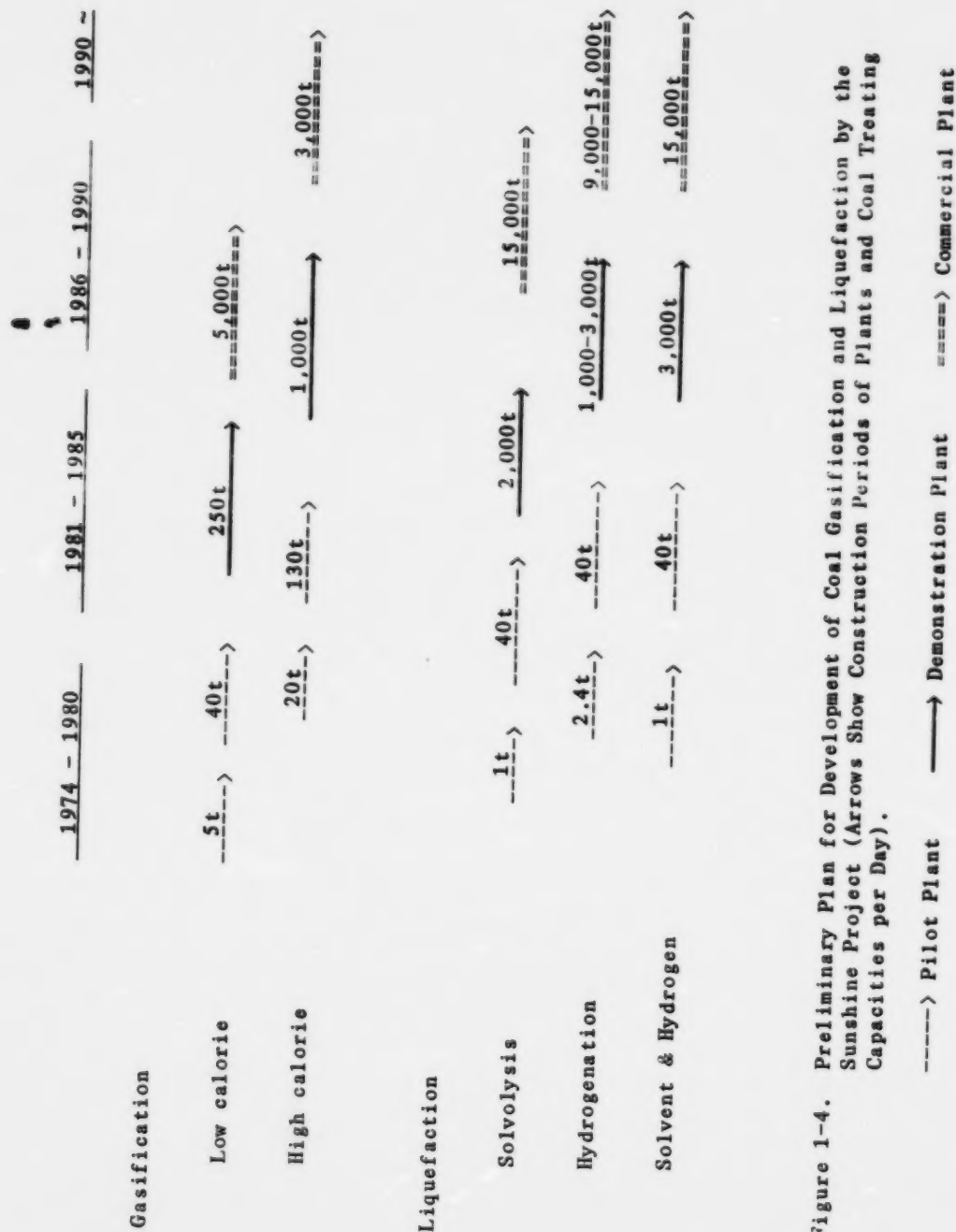


Figure 1-4. Preliminary Plan for Development of Coal Gasification and Liquefaction by the Sunshine Project (Arrows Show Construction Periods of Plants and Coal Treating Capacities per Day).

plants (Table 1-1 and Figure 1-3). It may be more appropriate for power plants to use more coal so that industry and cities can use larger amounts of LNG.

**Liquefaction:** It is not economically feasible to construct a liquefaction plant to produce fuel oil in Japan because of the necessity of importing coal. The primary objective of the liquefaction tests in Japan has been to produce a binder for coke production. When fuel oil from coal becomes necessary in the future, it would be more practical for liquefaction plants to be constructed abroad near large coal mines and the fuel oil exported to Japan.

Given these disadvantages as well as the technical and environmental problems, the Sunshine project plans shown in Figure 1-4 have been delayed, or in some cases, terminated. Although gasification and liquefaction may be needed in the future when the supply of oil and LNG becomes limited, further technological and economic improvements are needed before these technologies can be commercialized in Japan.

Many coal-fired boilers presently planned or under construction will use pulverized coal. Most of these boilers will use a wet limestone-gypsum FGD process and many will also use SCR.

## 1.2 AMBIENT NO<sub>2</sub> STANDARDS

The environmental quality standard for NO<sub>2</sub> in Japan was amended in 1978 from 0.02 ppm as a daily average to a new criterion of "within the range of 0.04-0.06 ppm as a daily average." The old standard was found to be overly stringent and not achievable in industrial regions and large cities. Under the new standard, NO<sub>2</sub> concentrations above 0.06 ppm, must be reduced to 0.06 ppm by 1985. In regions with NO<sub>2</sub> concentrations below 0.04 ppm, efforts must be made to keep NO<sub>2</sub> from exceeding 0.04 ppm.

The new daily average standards correspond to the annual NO<sub>2</sub> average of 0.02-0.03 ppm, a criterion proposed by the Expert Subcommittee on NO<sub>2</sub> of the Central Council for Environmental Pollution Control. At the same time it is



expected that an hourly average of 0.1-0.2 ppm, a short term criterion of the Subcommittee, can be met by the new standards.

There has been some criticism regarding the relaxation of the standards. The new standards, however, are still much more stringent than those of the U.S. and West Germany, which are equivalent to 0.05 ppm as a yearly average or 0.1 ppm as a daily average. As shown in Figures 1-5 and 1-6 and Table 1-2, NO<sub>2</sub> concentrations at some Japanese monitoring stations exceed the new standards although they meet the U.S. standards (based on the new Saltzman coefficient). Some of the prefectural governments have established more strict ambient air quality standards for NO<sub>2</sub>—0.04 ppm as a daily average—and have been trying to reduce NO<sub>2</sub> levels from the current 0.05-0.07 ppm to 0.04 ppm. Extensive NO<sub>x</sub> abatement efforts have been made so that both stationary and mobile sources can meet these standards.

### 1.3 NO<sub>x</sub> EMISSION STANDARDS FOR STATIONARY SOURCES

The NO<sub>x</sub> emission standards for stationary sources were first promulgated by the Central Government in 1973 to apply to large boilers and furnaces. These standards were revised in 1975, 1977, and 1979 to become more stringent and to cover a larger, more diverse number of emission sources (Table 1-3).

The NO<sub>x</sub> emission standards for major stationary sources are shown in Table 1-4. In addition to those shown in the table, emission standards have been applied to many other sources such as driers, calciners, smelters, reformers, generators, etc. Except in the case of nitric acid plants, NO<sub>x</sub> from these sources are derived from combustion, and therefore, the standards are based on the improved technology of combustion control described in Section 2. Industrial efforts described in the following sections have enabled these standards to be met.

Even with extensive NO<sub>x</sub> control for stationary sources and automobile exhausts (Section 1.4), it is not possible to meet the NO<sub>2</sub> ambient air quality standard in several regions which include large cities such as Tokyo and

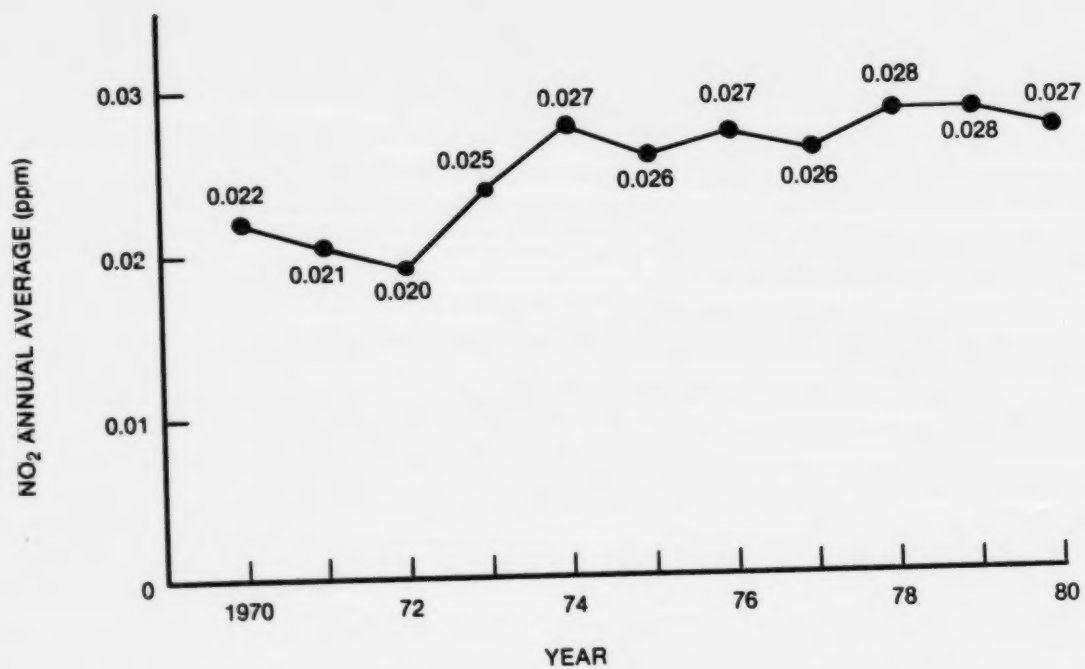


**Figure 1-5** Changes in Annual Average Concentration of NO<sub>2</sub>. (Average of those recorded at 15 general air pollution monitoring stations) (1).

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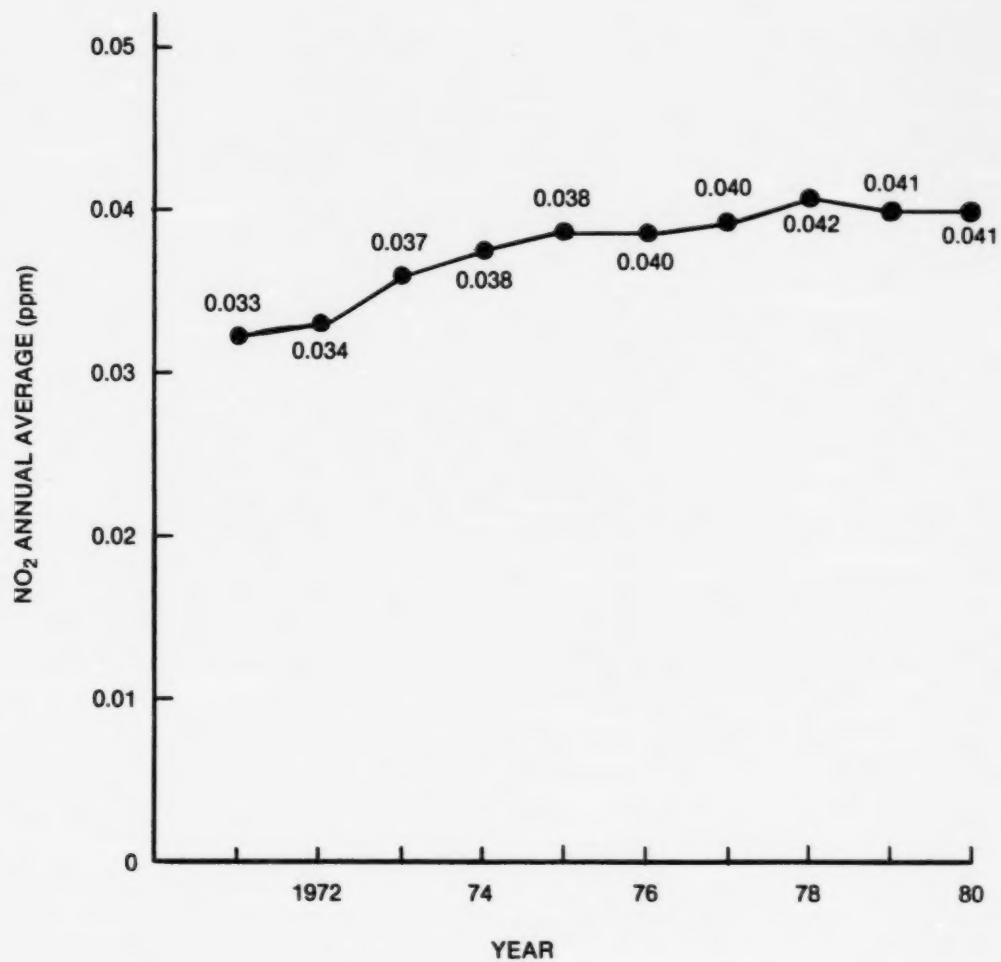


Figure 1-6 Changes in Annual Average Concentration of Nitrogen Dioxide.  
(average of 26 automobile pollution monitoring stations) (1)

TABLE 1-2. STATE OF COMPLIANCE WITH THE NEW NITROGEN DIOXIDE ENVIRONMENTAL QUALITY STANDARD IN 1978 (The data correspond to 98% of total readings)

| Descriptions of data corresponding to 98% of the total readings | Type of Monitoring Station               |            |                                         |            |
|-----------------------------------------------------------------|------------------------------------------|------------|-----------------------------------------|------------|
|                                                                 | General Air Pollution Monitoring Station |            | Automobile Pollution Monitoring Station |            |
|                                                                 | Number of stations                       | Percentage | Number of stations                      | Percentage |
| Recordings exceeding 0.06 ppm                                   | 75                                       | 7.6        | 77                                      | 40.5       |
| Recordings in the range 0.04 - 0.06 ppm                         | 233                                      | 23.8       | 92                                      | 48.4       |
| Recordings below 0.04 ppm                                       | 673                                      | 68.6       | 21                                      | 11.1       |
| Total                                                           | 981                                      | 100        | 190                                     | 100        |

Source: Environment Agency, Japan

TABLE 1-3. EXPANSION OF NO<sub>x</sub> CONTROL FOR STATIONARY SOURCES

|                                                                                                                    | 1973                                                   | 1975                                                                     | 1977                                                                                                       | 1979                                                                                      |
|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| NO <sub>x</sub> sources controlled (additions each year)                                                           | Large boilers and furnaces<br>HNO <sub>3</sub> plants. | Medium sized boilers and furnaces.<br>Large cement kilns and coke ovens. | Relatively small boilers and furnaces.<br>Medium sized cement kilns and coke ovens.<br>Waste incinerators. | Small boilers and furnaces.<br>Metal heating furnaces.<br>Gas generators, calciners, etc. |
| Number of sources controlled (total)                                                                               | 1,500                                                  | 3,400                                                                    | 13,000                                                                                                     | 105,000                                                                                   |
| NO <sub>x</sub> emitted from the controlled sources (percent of total NO <sub>x</sub> from all stationary sources) | 38                                                     | 44                                                                       | 73                                                                                                         | 95                                                                                        |

TABLE 1-4. NO<sub>x</sub> EMISSION STANDARDS FOR MAJOR STATIONARY SOURCES (ppm)

| Sources<br>(O <sub>2</sub> %)                       | Capacity<br>(1000 Nm <sup>3</sup> /hr) | ~1973            | 73-75            | 75-77            | 77-79            | 1979~ |
|-----------------------------------------------------|----------------------------------------|------------------|------------------|------------------|------------------|-------|
| Boiler (gas)<br>(5%)                                | >500                                   | 130              | 130              | 100              | 60               | 60    |
|                                                     | 100-500                                | 130              | 130              | 100              | 100              | 100   |
|                                                     | 40-100                                 | 130              | 130              | 130              | 100              | 100   |
|                                                     | 10-40                                  | 150              | 150              | 130              | 130              | 130   |
|                                                     | <10                                    | 150              | 150              | 150              | 150              | 150   |
| Boiler (oil)<br>(4%)                                | >500                                   | 180              | 180              | 150              | 130              | 130   |
|                                                     | 100-500                                | 170              | 180              | 150              | 150              | 150   |
|                                                     | 40-100                                 | 190              | 180              | 150              | 150              | 150   |
|                                                     | 10-40                                  | 210              | 230              | 150              | 150              | 150   |
|                                                     | 5-10                                   | 250              | 250              | 250              | 180              | 180   |
|                                                     | <5                                     | 250 <sup>a</sup> | 250 <sup>a</sup> | 250 <sup>a</sup> | 180              | 180   |
| Boiler (coal)<br>(6%)                               | >100                                   | 480              | 400              | 400              | 400              | 400   |
|                                                     | 40-100                                 | 600              | 480              | 480              | 400              | 400   |
|                                                     | 11-40                                  | 600              | 600              | 480              | 400              | 400   |
|                                                     | 5-10                                   | 480              | 480              | 480              | 400              | 400   |
|                                                     | <5                                     | 680 <sup>a</sup> | 480 <sup>a</sup> | 480 <sup>a</sup> | 400              | 400   |
| Sintering<br>Machine                                | >100                                   | 260              | 260              | 260              | 220              | 220   |
|                                                     | 10-100                                 | 270 <sup>b</sup> | 270 <sup>b</sup> | 270 <sup>b</sup> | 220              | 220   |
|                                                     | <10                                    | 300 <sup>b</sup> | 300 <sup>b</sup> | 300 <sup>b</sup> | 300 <sup>b</sup> | 220   |
| Metal heating<br>furnace<br>(Radiant type)<br>(11%) | >100                                   | 200              | 200              | 100              | 100              | 100   |
|                                                     | 40-100                                 | 200              | 200              | 150              | 150              | 150   |
|                                                     | 10-40                                  | 200              | 200              | 150              | 150              | 150   |
|                                                     | 5-10                                   | 200              | 200              | 200              | 150              | 150   |
|                                                     | <5                                     | 200 <sup>b</sup> | 200 <sup>b</sup> | 200 <sup>b</sup> | 180              | 180   |
| Petroleum<br>heating<br>furnace (6%)                | >40                                    | 170              | 170              | 100              | 100              | 100   |
|                                                     | 10-40                                  | 180              | 150              | 150              | 130              | 130   |
|                                                     | 5-10                                   | 180              | 180              | 180              | 150              | 150   |
|                                                     | <5                                     | 200              | 200              | 200              | 180              | 180   |
| Cement Kiln<br>(10%)                                | >100                                   | 480              | 480              | 250              | 250              | 250   |
|                                                     | <100                                   | 480              | 480              | 480              | 350              | 350   |
| Glass furnace<br>(15%)                              |                                        | 500              | 500              | 500              | 500              | 450   |
| Waste<br>incinerator<br>(12%)                       | >40                                    | 300 <sup>b</sup> | 300 <sup>b</sup> | 300 <sup>b</sup> | 250              | 250   |
|                                                     | <40                                    | 300 <sup>b</sup> | 300 <sup>b</sup> | 300 <sup>b</sup> | 300 <sup>b</sup> | 250   |
| Coke oven<br>(7%)                                   | >100                                   | 350              | 350              | 200              | 170              | 170   |
|                                                     | <100                                   | 350              | 350              | 350              | 170              | 170   |
| Nitric acid<br>plant                                |                                        | 200              | 200              | 200              | 200              | 200   |

<sup>a</sup>To be met by 1984.<sup>b</sup>To be met by 1982.



Osaka. Therefore, the Central Government (Environment Agency) decided to apply total emission regulations to Tokyo, Osaka, and Yokohama in order to further increase NO<sub>x</sub> abatement and meet the air quality standard. Similar total emission regulations for SO<sub>x</sub> have been successfully applied in several regions and have resulted in the attainment of the SO<sub>2</sub> air quality standard. The NO<sub>x</sub> regulations are more difficult to attain because over 50% of NO<sub>x</sub> emissions in most large cities are derived from mobile sources, while most SO<sub>x</sub> emissions are from stationary sources. With implementation of the total emission regulations as well as stringent local regulations, flue gas treatment for NO<sub>x</sub> removal will be needed in addition to combustion modification.

#### 1.4 NO<sub>x</sub> CONTROL FOR MOBILE SOURCES

The emission standards for gasoline engine passenger cars are shown in Table 1-5. According to the 1978 standards, NO<sub>x</sub> discharge is controlled below 0.25 g/km, on the average. Accordingly, permissible limits are set at 0.48 g/km, as shown in Table 1-5. At the same time, those in 11 modes are limited to 6.0 g/test (average discharge 4.4 g/test). The 1978 standard is responsible for a 60-70 percent reduction in NO<sub>x</sub> discharge compared with the 1976 regulations and to over a 90 percent reduction compared with the time when there were no regulations. The 1978 standards are much more stringent than similar standards in the U.S. (Table 1-6).

It was predicted that automobile performance and fuel economy would decline measurably with enactment of the 1978 standards. However, strenuous efforts have been made to maintain and even to improve fuel economy while maintaining performance. As the result of these efforts, fuel consumption rates have improved considerably in the vehicles which satisfy the 1978 standards. Fuel economy for some models is lower than that of automobiles which complied with the 1973 standards.

The NO<sub>x</sub> regulations for heavy duty diesel engine vehicles (buses and trucks) have also been tightened (Table 1-7). Under the 1977 regulation, NO<sub>x</sub> emissions from diesel vehicles were reduced by about 30% while those

TABLE 1-5. AUTOMOBILE EMISSION STANDARDS IN JAPAN<sup>a</sup>

|      | HC<br>(g/km) | CO<br>(g/km)  | NO <sub>x</sub><br>(g/km) |
|------|--------------|---------------|---------------------------|
| 1973 | 3.80 (2.94)  | 28.00 (18.40) | 3.00 (2.18)               |
| 1975 | 0.39 (0.25)  | 2.70 (2.10)   | 1.60 (1.20)               |
| 1976 | 0.39 (0.25)  | 2.70 (2.10)   | 0.84 (0.60)               |
| 1978 | 0.39 (0.25)  | 2.70 (2.10)   | 0.48 (0.25)               |

<sup>a</sup>Figures show allowable limits; those in parentheses indicate average emissions.

TABLE 1-6. AUTOMOBILE EMISSION STANDARDS IN THE UNITED STATES<sup>a</sup>

|      | HC<br>(g/km) | CO<br>(g/km) | NO <sub>x</sub><br>(g/km) |
|------|--------------|--------------|---------------------------|
| 1978 | 0.94         | 9.4          | 1.25                      |
| 1979 | 0.94         | 9.4          | 1.25                      |
| 1980 | 0.26         | 4.4          | 1.25                      |
| 1981 | 0.26         | 2.1          | 0.63                      |

<sup>a</sup>Established by the Clean Air Act of 1977.

from gasoline engine and LPG engine heavy duty vehicles were reduced by about 45%—as compared with the uncontrolled emissions in 1973.

With these regulations and efforts to reduce traffic by 10%, the  $\text{NO}_x$  emissions from automobiles will be reduced by about 40% by 1983; but will increase after 1984 due to projected increases in traffic (Figure 1-7). The 1978 standard for gasoline engine passenger cars will not be amended. However,  $\text{NO}_x$  control for diesel engine vehicles will be tightened (Tables 1-7 and 1-8).

TABLE 1-7. EMISSION STANDARDS FOR DIESEL ENGINE HEAVY DUTY VEHICLES (PPM)

|      | CO  | HC  | $\text{NO}_x$          |                       |
|------|-----|-----|------------------------|-----------------------|
|      |     |     | Auxiliary Chamber Type | Direct Injection Type |
| 1974 | 980 | 670 | 590                    | 1000                  |
| 1977 | 980 | 670 | 500                    | 850                   |
| 1979 | 980 | 670 | 450                    | 700                   |
| 1981 |     |     | 450                    | 540                   |
| 1983 |     |     | 290                    | 470                   |

TABLE 1-8.  $\text{NO}_x$  CONTROL FOR DIESEL ENGINE PASSENGER CARS (g/km)

|             | Current Regulation | Interim Target | Target |
|-------------|--------------------|----------------|--------|
| Medium Size | 1.2                | 0.9            | 0.6    |
| Small Size  | 1.0                | 0.7            | 0.5    |

#### 1.5 METHODS OF $\text{NO}_x$ ABATEMENT FOR STATIONARY SOURCES

The major methods of  $\text{NO}_x$  abatement for stationary sources are classified in Table 1-9.

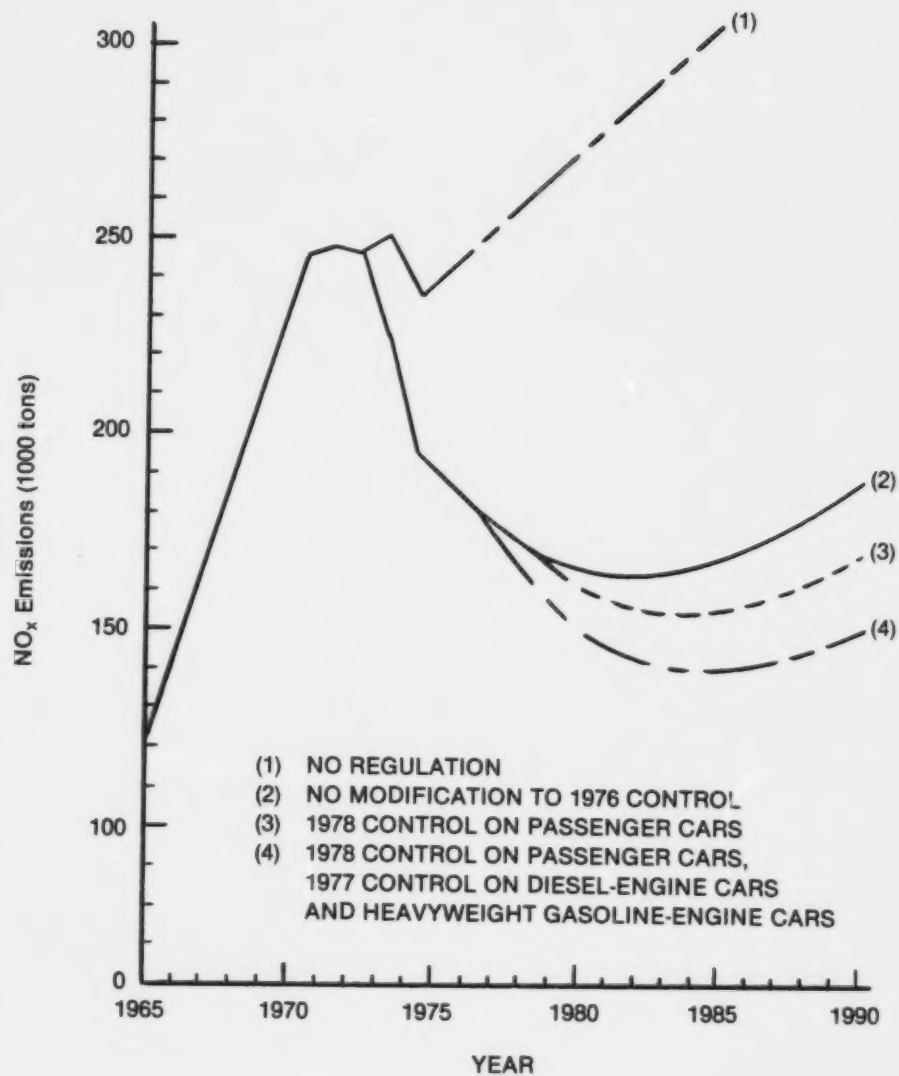


Figure 1-7 Estimated Total Amount of NO<sub>x</sub> Emissions from Road Traffic in the Tokyo Bay Area. (2)

TABLE 1-9. CLASSIFICATION OF NO<sub>x</sub> ABATEMENT METHODS

|                         |               |                                     |                                                                                                                                        |
|-------------------------|---------------|-------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| Reduction of Formation  | [             | Combustion Modification             | [ Low Oxygen Combustion<br>Flue Gas Recirculation<br>Staged Combustion<br>Off-Stoichiometric Combustion<br>Low NO <sub>x</sub> Burners |
|                         |               | Use of Low-Nitrogen Fuel            | [ Change of Fuel<br>Nitrogen Removal from Fuel                                                                                         |
| NO <sub>x</sub> Removal | [ Dry Process | NO <sub>x</sub> only                | [ Selective Catalytic Reduction (SNR)<br>Selective Noncatalytic Reduction (SNR)<br>In-furnace Reduction                                |
|                         |               | SO <sub>x</sub> and NO <sub>x</sub> | [ Carbon Adsorption<br>Copper Oxide Adsorption<br>Electron Beam Radiation                                                              |
|                         | [ Wet Process | NO <sub>x</sub> only                | [ Oxidation Absorption                                                                                                                 |
|                         |               | SO <sub>x</sub> and NO <sub>x</sub> | [ Oxidation Reduction<br>Absorption Reduction                                                                                          |

Combustion modification is the most reasonable first step for stationary source NO<sub>x</sub> abatement. It is described in more detail in Section 2. Combustion modification has been widely applied in Japan and has reduced NO<sub>x</sub> by 20-70 percent from each stationary source.

A widespread switch from high-nitrogen to low-nitrogen fuel has occurred in Japan. Heavy oil, now the major fuel, usually contains 0.2-0.3 percent nitrogen, and its combustion gas contains 100-130 ppm of NO<sub>x</sub> using the best combustion control. Hydrodesulfurization of heavy oil, which removes 70-90 percent of sulfur, also removes 20-30 percent of the nitrogen and contributes to NO<sub>x</sub> reduction by 20-30 ppm. Kerosene is used in many small stationary sources.



A considerable number of power plants constructed recently near large cities burn LNG (imported liquid natural gas), which produces only 30-40 ppm of  $\text{NO}_x$  using the best combustion control. However, there is, a limit to the supply of such clean fuel, and it is expensive as well.

Recently it has become necessary to use increasing amounts of coal, particularly for power generation. Since coal contains over 1% nitrogen and produces flue gas with about 200 ppm  $\text{NO}_x$ , even using combustion modification, flue gas treatment may be needed for further  $\text{NO}_x$  reduction.

Many processes have been developed to remove  $\text{NO}_x$  from flue gas. Of these, a selective catalytic reduction (SCR) process that uses  $\text{NH}_3$  and a catalyst at 300-400°C to reduce  $\text{NO}_x$  to  $\text{N}_2$  has been the most widely used. SCR is simple, has a high  $\text{NO}_x$  removal efficiency of 80-90%, and does not produce by-products which present difficult disposal problems. Although  $\text{NO}_x$  can be reduced to  $\text{N}_2$  by other reducing agent gases such as  $\text{H}_2$ , CO, and  $\text{CH}_4$ , large amounts of these gases are consumed by reacting with the  $\text{O}_2$  in flue gas. The use of  $\text{NH}_3$  is more suitable because it selectively reacts with  $\text{NO}_x$  (Section 3). SCR was initially applied to industrial boilers and furnaces (Figure 1-8). Since 1978, many large SCR units have been constructed for utility boilers (Table 4-1, Section 4).

Selective noncatalytic reduction (SNR),  $\text{NH}_3$  reduction without a catalyst, also has been used commercially. SNR is simpler than SCR, but its  $\text{NO}_x$  removal efficiency rarely exceeds 50 percent and a considerable amount of  $\text{NH}_3$  is emitted (see Section 6.2).

In-furnace  $\text{NO}_x$  reduction has been developed recently and applied to small oil-fired utility boilers to remove about 50% of  $\text{NO}_x$ . With this process, a small amount of fuel, about 10% of that used for the boiler, is injected above the flame in the furnace and then has air added to it for complete combustion. The size of this furnace is 10 to 20% larger than a conventional furnace (see Section 6.4).

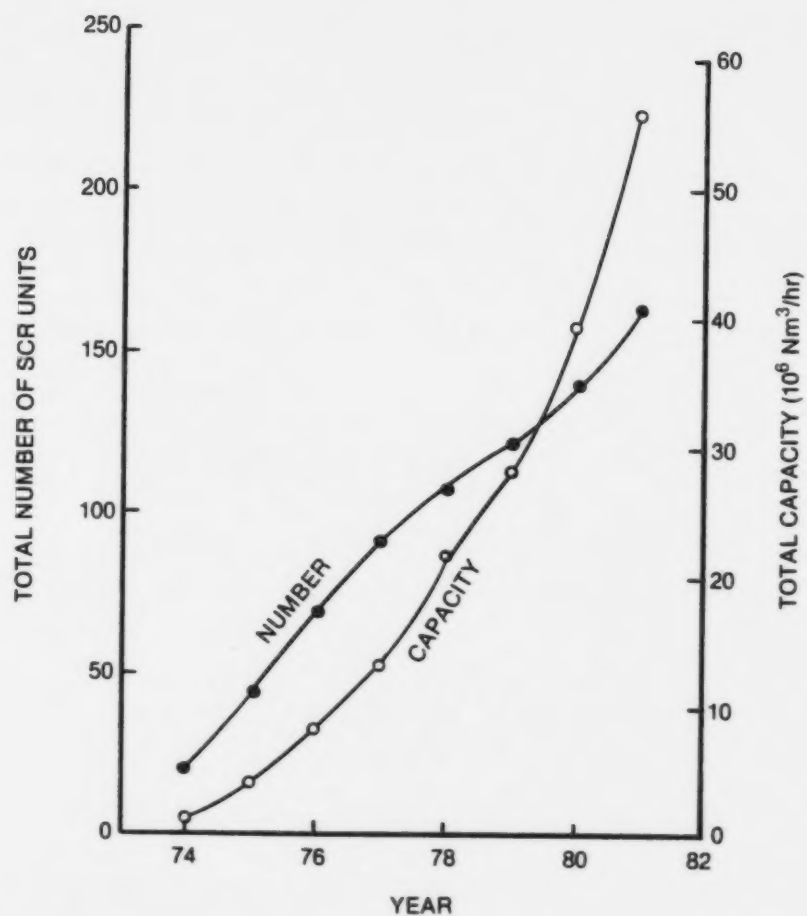


**Figure 1-8** Number and Total Capacity of NO<sub>x</sub> Selective Catalytic Reduction (SCR) Plants: 1974 - 1981.

Among dry  $\text{SO}_x$  and  $\text{NO}_x$  removal processes, carbon adsorption and electron beam processes have been tested at a pilot plant while a copper oxide adsorption process has been used for an industrial boiler. The carbon and copper oxide processes use ammonia to decompose  $\text{NO}_x$  to  $\text{N}_2$  and  $\text{H}_2\text{O}$ ; the electron beam process forms ammonium nitrate and ammonium sulfate byproducts which are used for fertilizer.

The disadvantage of wet processes is that they require extensive wastewater treatment to eliminate nitrate and other compounds. Efforts have been made to recover useful byproducts and to minimize the amount of wastewater produced.

## 1.6 LOCAL REGULATIONS AND $\text{NO}_x$ ABATEMENT

### 1.6.1 Introduction

Prefectural governments and large city authorities have established pollution control ordinances for stationary sources which are usually much more stringent than those set by the Central Government. In addition, city authorities and citizens groups often make agreements with industries for further pollution control. A good example of the way in which local pollution control regulatory agencies operate is the Kanagawa Prefecture.

Kanagawa Prefecture adjacent to Tokyo has an area of 2,391  $\text{km}^2$  and three major cities—Yokohama, Kawasaki, and Yokosuka with populations of about 4 million, 1 million, and 400,000, respectively (Figure 1-9). These cities have numerous industries including several electric power stations, steel works, and oil refineries.

The first step towards pollution control was taken in 1951 with the enactment of the Kanagawa Prefectural Workshop Pollution Prevention Ordinance. The ordinance was revised in 1955, 1971, and 1978 to comprise the present Kanagawa Prefectural Ordinance for Pollution Control.

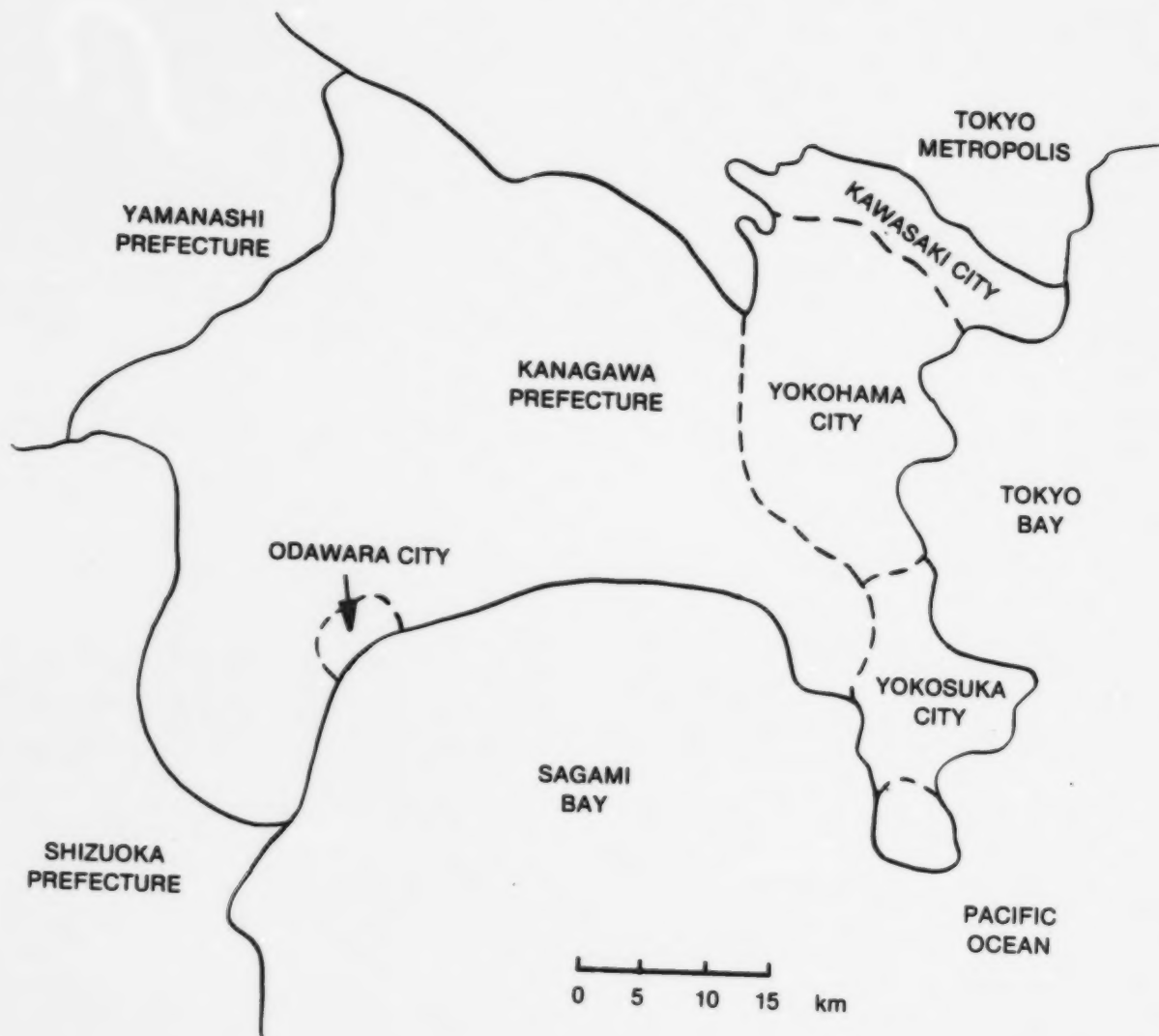


**Figure 1-9** Kanagawa Prefecture and its Major Cities.

### 1.6.2 Air Quality Monitoring Systems in the Kanagawa Prefecture

The three major cities in Kanagawa have installed their own monitoring systems with automatic analyzer-telemeter-computer systems for measuring, recording, and analyzing pollutants in ambient air, automobile exhausts, and stack emissions. For example, Yokohama City has 12 ambient air monitoring stations for measuring  $\text{SO}_2$ , suspended particulates,  $\text{NO}$ ,  $\text{NO}_2$ , and oxidants as well as wind velocity and direction; eight automobile exhaust monitoring stations for suspended particulates,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HC}$ , oxidants, as well as the number of passing cars; and stack gas monitoring systems to analyze  $\text{SO}_x$ ,  $\text{NO}_x$ , and particulates at 40 major stationary sources. All of the analytical results are transmitted to the Yokohama City Office on an hourly basis.

In addition, Kanagawa Prefecture has its own ambient air and automobile exhaust monitoring stations in areas other than the three cities. Information from a total of 72 monitoring stations, including the stations owned by the cities, are transmitted to the Prefecture's air monitoring center. The annual costs for the center are shown in Table 1-10.

The initial air quality control efforts in Kanagawa focused on  $\text{SO}_x$  abatement. Since the ambient  $\text{SO}_2$  concentrations now have been reduced to meet the standard (0.04 ppm daily average) at most of the monitoring stations, recent efforts have been concentrated on  $\text{NO}_x$  control.

The daily average  $\text{NO}_2$  concentrations at some of the stations in the three cities sometimes exceeds the 0.06 ppm national standard. Kanagawa Prefecture has been making efforts to reduce the concentrations to 0.04 ppm by extensive  $\text{NO}_x$  reduction.

### 1.6.3 $\text{NO}_x$ Emissions and Control in Kanagawa Prefecture

In the city of Yokohama, about 65% of the total  $\text{NO}_x$  emissions are derived from stationary sources while about 30% come from automobiles. The latter is controlled by the national regulation; stationary source emissions are regulated by prefectural ordinances and agreements between the Prefecture or



TABLE 1-10. TOTAL COST FOR KANAGAWA CONTINUOUS AIR MONITORING CENTER (1970-1980)

| Items/Year | Measuring Sets |                | Telemetry      |                | Others         |                |
|------------|----------------|----------------|----------------|----------------|----------------|----------------|
|            | Purchase       | Operating      | Purchase       | Operating      | Purchase       | Operating      |
|            | Cost (\$1,000) | Cost (\$1,000) | Cost (\$1,000) | Cost (\$1,000) | Cost (\$1,000) | Cost (\$1,000) |
| 1970       | 1624           | —              | 23             | —              | 50             | —              |
| 1971       | 307            | 109            | 169            | 22             | —              | 1              |
| 1972       | 192            | 144            | 670            | 26             | 154            | 2              |
| 1973       | 172            | 220            | 947            | 13             | —              | 9              |
| 1974       | 144            | 176            | 74             | 23             | 4              | 30             |
| 1975       | 21             | 326            | —              | 123            | —              | 35             |
| 1976       | 29             | 304            | —              | 133            | —              | 35             |
| 1977       | 455            | 361            | —              | 158            | 32             | 33             |
| 1978       | 672            | 361            | —              | 160            | 8              | 36             |
| 1979       | 301            | 399            | —              | 149            | 7              | 39             |
| 1980       | 166            | 444            | 402            | 141            | —              | 39             |
| TOTAL      | 4,083          | 2,844          | 2,498          | 948            | 255            | 259            |
| TOTAL      |                | 6,927          |                | 3,446          |                | 514            |
|            |                |                |                |                |                | 10,887         |

City and industry. Yokohama has 1,165 plants which use more than 1 kiloliter of oil per hour including 13 large plants (three utility power stations, three oil refineries, two glass plants, etc.) that emit about 95% of the  $\text{NO}_x$  from all stationary sources. As a whole, a 64% reduction of the 1974  $\text{NO}_x$  emissions must be achieved to attain 0.04 ppm as a daily average. Therefore, 60-70%  $\text{NO}_x$  reduction of the 1974 emissions is requested of the large plants and a 30-50% reduction of the smaller plants. Since these reductions are not easily achieved by combustion modification, a considerable number of plants must remove  $\text{NO}_x$  from flue gas. According to the City's initial plan, the reduction was to be achieved by 1981. This time limit has been postponed 2 years because it was too difficult to meet.

Yokohama has 3 power stations—Yokohama Power Station which burns oil and Minamiyokohama Power Station (LNG), both belonging to Tokyo Electric, and EPDC's Isogo Power Station which burns coal. The  $\text{NO}_x$  emissions and regulations which apply to these utility boilers are compared in Table 1-11.

TABLE 1-11.  $\text{NO}_x$  EMISSIONS AND REGULATIONS FOR EXISTING UTILITY BOILERS IN YOKOHAMA CITY

| Fuel | YOKOHAMA CITY (PPM)            |                            |                    |                   |
|------|--------------------------------|----------------------------|--------------------|-------------------|
|      | Before $\text{NO}_x$ abatement | Present level <sup>a</sup> | Central government | Yokohama (Target) |
| Gas  | 150-250                        | 40-80                      | 130                | 50                |
| Oil  | 250-350                        | 80-150                     | 180                | 80                |
| Coal | 400-600                        | 160-200                    | 400                | 159               |

<sup>a</sup>Achieved by combustion modification

The target  $\text{NO}_x$  concentration chosen by Yokohama City is less than one-half the emission standard set by the Central Government and is not easily achievable by combustion modification alone. Yokosuka and Kawasaki Cities also have set similarly stringent  $\text{NO}_x$  target concentrations. In order to meet these targets, 7 SCR plants are in operation for various gas sources,

TABLE 1-12. NO<sub>x</sub> REMOVAL PLANTS IN KANAGAWA PREFECTURE

| Owner                  | Plant Site | Gas Source        | Gas Treated<br>(1,000 Nm <sup>3</sup> /hr) | Process               | Year<br>Completed |
|------------------------|------------|-------------------|--------------------------------------------|-----------------------|-------------------|
| Asahi Glass            | Yokohama   | Glass furnace     | 75                                         | SCR <sup>a</sup>      | 1976              |
| Tokyo Electric<br>"    | Yokohama   | Oil-fired boiler  | 500                                        | SNR <sup>b</sup> +SCR | 1978 <sup>d</sup> |
|                        | Yokosuka   | "                 | 1060                                       | SNR+SCR               | 1978 <sup>d</sup> |
| Nippon Kokan           | Kawasaki   | Sintering machine | 1300                                       | SCR                   | 1979              |
| Ajinomoto              | Kawasaki   | Oil-fired boiler  | 180                                        | SCR                   | 1978              |
| Nippon Yakin           | Kawasaki   | Oil-fired boiler  | 15                                         | SCR                   | 1976              |
| Toho Gas               | Kawasaki   | Gas generator     | 10                                         | SCR                   | 1976              |
| Tonen Sekiyu<br>Kagaku | Kawasaki   | Oil-fired boiler  | 423                                        | SNR <sup>c</sup>      | 1976              |
| Tonen Sekiyu<br>Kagaku | Kawasaki   | Oil-fired boiler  | 423                                        | SNR <sup>c</sup>      | 1977              |
| Toa Nenryo             | Kawasaki   | CO boiler         | 314                                        | SNR <sup>c</sup>      | 1978              |
| Toa Nenryo             | Kawasaki   | Pipestill furnace | 254                                        | SNR <sup>c</sup>      | 1978              |

<sup>a</sup>Selective catalytic reduction<sup>b</sup>Selective noncatalytic reduction<sup>c</sup>Selective noncatalytic reduction for emergency use<sup>d</sup>Demonstration Plant. The SNR system was removed in 1980.

while four plants using selective noncatalytic reduction (Thermal DeNO<sub>x</sub>) have been installed for emergency use (Table 1-12).

The NO<sub>x</sub> concentrations in the flue gas from the coal-fired boilers at EDPC's Isogo Station, has been lowered from 400-500 ppm to 160-180 ppm by combustion modification. Although the City has requested further NO<sub>x</sub> reduction the power station has no space to install a NO<sub>x</sub> removal facility because FGD plants were retrofitted in the narrow space beside the boilers. Therefore, efforts have been continued for further NO<sub>x</sub> abatement by combustion modification.

#### 1.7 AIR POLLUTION PROBLEMS RELATED TO NO<sub>x</sub>

In Japan, ambient SO<sub>2</sub> concentrations have been lowered substantially in order to meet the stringent standards (Figure 1-10 and Table 1-13). On the other hand, the number of designated air pollution patients have increased (Figure 1-10). Designated patients are the inhabitants of specific polluted regions such as Yokohama, Kawasaki, Amagasaki and portions of Tokyo and Osaka who have been diagnosed as air pollution victims. They receive compensation from the government for medical care and living expenses.

TABLE 1-13. AMBIENT AIR QUALITY STANDARDS (ppm)

|              | SO <sub>2</sub> |        | NO <sub>2</sub>                             |                                               |
|--------------|-----------------|--------|---------------------------------------------|-----------------------------------------------|
|              | Daily           | Yearly | Daily                                       | Yearly                                        |
| Japan        | 0.04            | (0.02) | 0.02 <sup>a</sup><br>0.04-0.06 <sup>b</sup> | 0.01 <sup>a</sup><br>(0.02-0.03) <sup>b</sup> |
| U.S.A.       |                 | 0.03   |                                             | 0.05                                          |
| West Germany |                 | 0.05   |                                             | 0.05                                          |

<sup>a</sup>1973-1978

<sup>b</sup>Since 1979

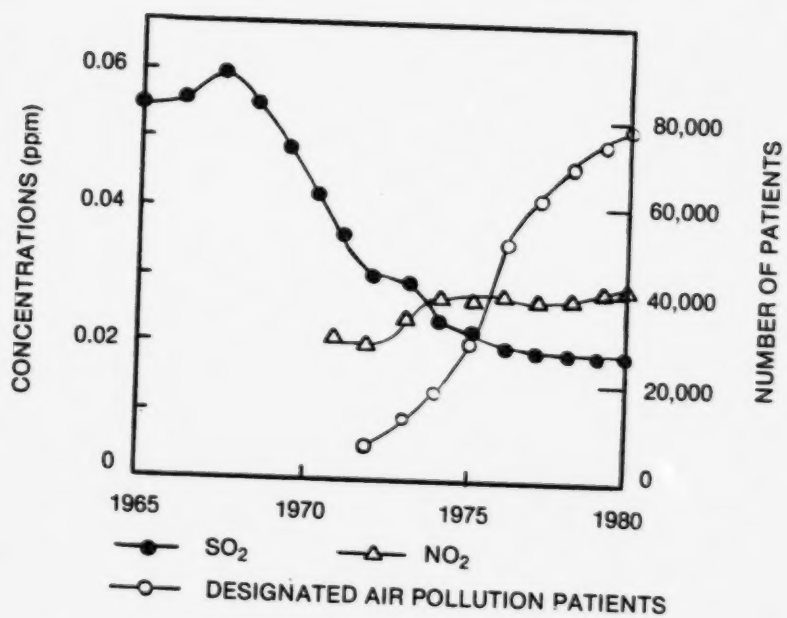


**Figure 1-10 Annual Average Ambient SO<sub>2</sub> Concentrations in 15 Major Cities and Industrial Regions and Number of Designated Air Pollution Patients.**

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The major reason for the increase in patients is the expansion of the designated regions to include several regions of Tokyo and Osaka. As ambient  $\text{NO}_2$  concentrations have increased considerably between 1970 and 1974 and slightly since 1978, some people claim that the increase in patients is caused by ambient  $\text{NO}_2$  concentrations. Although the  $\text{NO}_2$  concentrations exceed the standard in several regions,  $\text{NO}_2$  may not be the direct cause of patient increases; the concentrations are well below the U.S. standard.

A number of problems with photochemical smog were encountered in 1973-1974 but these have decreased since that time (Table 1-14). The decrease may be related to the decrease in hydrocarbon emissions (Table 1-15). Particulate emissions from stationary sources also have been reduced substantially.

It should be noted that the annual average ambient sulfate concentrations in five major cities (Tokyo, Kawasaki, Osaka, Amagasaki, and Kitakyushu), decreased from  $30\mu\text{g}/\text{m}^3$  in 1970 to  $13\mu\text{g}/\text{m}^3$  in 1973. Since then the concentrations have increased slightly to  $15\mu\text{g}/\text{m}^3$  in 1979, despite an on-going decrease in ambient  $\text{SO}_2$  concentrations. This may be due to the increase in diesel cars which emit sulfuric acid mists and also possibly to the slight increase in  $\text{NO}_x$  which tends to promote the oxidation of  $\text{SO}_2$  to sulfate.

Although sulfate concentrations since 1973 have not been high, the sulfuric acid mists from diesel cars may affect human health in Japan where there are many diesel buses and trucks and the sulfur content in the light oil for diesel engines already is high (0.4% as compared with about 0.2% in the U.S.). Sulfur abatement of the light oil and further control of particulates for diesel-engine exhausts may be needed.

TABLE 1-14. NUMBER OF DAYS IN WHICH PHOTOCHEMICAL SMOG WARNINGS WERE ISSUED (1)

| Area            | Prefecture | 1970 | '71 | '72 | '73 | '74 | '75 | '76 | '77 | '78 | '79 | '80 | '81 |
|-----------------|------------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Tokyo Bay       | Saitama    |      | 23  | 15  | 45  | 29  | 44  | 15  | 26  | 36  | 8   | 15  | 8   |
|                 | Chiba      |      | 19  | 21  | 28  | 26  | 33  | 21  | 7   | 14  | 11  | 13  | 8   |
|                 | Tokyo      | 7    | 33  | 33  | 45  | 26  | 41  | 17  | 21  | 22  | 12  | 13  | 14  |
|                 | Kanagawa   |      | 11  | 31  | 30  | 26  | 27  | 17  | 12  | 18  | 19  | 10  | 11  |
| Osaka Bay       | Kyoto      |      |     | 7   | 17  | 17  | 11  | 6   | 9   | 5   | 1   | 5   | 3   |
|                 | Osaka      |      | 4   | 18  | 26  | 27  | 23  | 25  | 25  | 16  | 12  | 10  | 12  |
|                 | Hyogo      |      | 7   | 19  | 23  | 19  | 11  | 3   | 4   | 2   | 1   | 1   | 1   |
|                 | Nara       |      |     | 1   | 6   | 3   | 9   | 3   | 3   | 3   |     | 1   |     |
| Seto Inland Sea | Okayama    |      | 3   | 14  | 14  | 16  | 5   | 1   | 5   | 8   | 1   | 1   |     |
|                 | Hirashima  |      |     | 9   | 18  | 18  | 4   |     | 6   | 9   | 1   | 1   |     |
|                 | Yamaguchi  |      |     |     |     | 5   | 1   |     | 5   | 3   |     |     |     |
|                 | Tokushima  |      |     |     |     | 2   | 2   |     | 3   | 1   |     |     |     |
|                 | Kagawa     |      |     |     | 1   | 4   | 1   |     |     | 6   |     |     |     |
|                 | Ehime      |      |     | 2   | 2   | 13  | 1   | 4   | 7   | 1   | 2   | 1   |     |
| Ise Bay         | Aichi      |      | 1   | 5   | 8   | 2   | 6   | 3   | 2   |     | 1   |     |     |
|                 | Mie        |      |     | 4   | 6   | 7   |     | 3   | 1   |     |     |     |     |
| TOTAL*          |            | 7    | 98  | 176 | 328 | 288 | 260 | 150 | 187 | 189 | 84  | 72  | 57  |

\*Including other prefectures

TABLE 1-15. GASEOUS HYDROCARBON EMISSIONS FROM STATIONARY SOURCES (1)

| Sources          | 1973          |                       |              | 1978          |              |              |
|------------------|---------------|-----------------------|--------------|---------------|--------------|--------------|
|                  | Amount<br>(t) | Ratio<br>(% of total) | Ratio<br>(%) | Amount<br>(t) | Ratio<br>(%) | Ratio<br>(%) |
| Petroleum        |               |                       |              |               |              |              |
| Refinery         | 67,000        | 5.2                   |              | 42,400        | 4.0          |              |
| Service Tank     | 68,100        | 5.2                   | 15.2         | 41,800        | 3.7          | 14.6         |
| Service Station  | 62,800        | 4.8                   |              | 78,500        | 6.9          |              |
| Others           | 100           |                       |              | 100           |              |              |
| Petrochemical    |               |                       |              |               |              |              |
| Plant            | 69,800        | 5.4                   |              | 27,000        | 2.4          |              |
| Tank             | 4,900         | 0.4                   | 5.8          | 3,600         | 0.3          | 2.7          |
| Painting         |               |                       |              |               |              |              |
| Production       | 1,600         | 0.1                   |              | 1,500         | 0.1          |              |
| Car Painting     | 37,500        | 2.9                   |              | 45,400        | 4.1          |              |
| Ship Painting    | 19,900        | 1.5                   | 47.9         | 16,700        | 1.5          | 55.2         |
| Others           | 564,500       | 43.4                  |              | 552,800       | 49.5         |              |
| Inks             | 109,800       | 8.4                   | 8.4          | 81,100        | 7.2          | 7.2          |
| Other Solvents   |               |                       |              |               |              |              |
| Cementing        | 42,500        | 3.3                   |              | 32,800        | 2.9          |              |
| Metal degreasing | 85,000        | 6.5                   |              | 52,800        | 4.7          |              |
| Cleaning         | 116,500       | 9.0                   | 22.7         | 106,000       | 9.5          | 20.3         |
| Rubber           | 51,200        | 3.9                   |              | 35,000        | 3.1          |              |
| TOTAL            | 1,301,200     | 100.0                 | 100.0        | 1,117,600     | 100.0        | 100.0        |

#### REFERENCES

1. Environment Agency. White Paper on Environment, 1982 (in Japanese).
2. Environment Agency. Recent Countermeasures for Air Pollution Control in Japan, 1977 (After OECD Review of Japanese Environmental Politics in 1976).

## SECTION 2

### NO<sub>x</sub> ABATEMENT BY COMBUSTION MODIFICATION (CM)

#### 2.1 INTRODUCTION

##### 2.1.1 Classification of Combustion Modification (CM) Techniques

NO<sub>x</sub> emissions from combustion processes consist of thermal NO<sub>x</sub> formed by the oxidation of nitrogen in air at high temperatures and fuel NO<sub>x</sub> derived from nitrogen compounds in fuel. Thermal NO<sub>x</sub> can be reduced by combustion modifications, such as decreasing the oxygen concentration in the combustion regions; shortening the residence time of combustion gases in high temperature zones; or lowering the flame temperature. Fuel NO<sub>x</sub> emissions can be reduced by decreasing the oxygen concentration in the combustion reaction zone and by switching to a low-nitrogen fuel.

Combustion modification techniques used widely in Japan for NO<sub>x</sub> control can be grouped into four categories:

- Modified operating conditions
  - 1) Low-excess-air combustion
  - 2) Change of fuel/air contacting in the combustion chamber
  - 3) Reduction of heat load in combustion chamber (reduction of output power)
  - 4) Lowering of air preheating temperature
- Burner design modification



- Modifications in combustion system design
  - 1) Reduction of heat density in combustion chamber (increased furnace volume)
  - 2) Staged combustion
  - 3) Flue gas recirculation
  - 4) Water or steam injection
- Other methods
  - 1) Fuel switching
  - 2) Firing modification

Many combinations of the above techniques have also been used. Although operating conditions can be changed relatively easily in existing installations, the changes usually reduce  $\text{NO}_x$  emissions only slightly and often cause operating problems. On the other hand, modifications in burner and combustion system design are promising control techniques. Fewer problems are encountered when design modifications are incorporated in new plants; relatively large reconstruction costs are required when the modifications are applied to existing installations.

In Japan,  $\text{NO}_x$  emission limits have been applied to over 100,000 sources including boilers, various furnaces and kilns, heaters, and incinerators, representing about 95% of the total emissions from all stationary sources (Section 1.3). Virtually all of these sources have reduced  $\text{NO}_x$  emissions by combustion modification. Larger sources use the combination of staged combustion, flue gas recirculation (gas mixing) and low- $\text{NO}_x$  burners (Table 2-1) while smaller sources reduce  $\text{NO}_x$  primarily with low- $\text{NO}_x$  burners and fuel switching.

With these efforts,  $\text{NO}_x$  concentrations in boiler flue gases have been maintained at 30-120 ppm for gas-, 60-200 ppm for oil-, and 150-400 ppm for coal-firing to meet the national emission standards and the more stringent local regulations (Table 2-1). For further  $\text{NO}_x$  reduction, over 160 SCR plants are in operation or under construction. Normally SCR is applied in combination with combustion modification.

TABLE 2-1. NUMBER OF BOILERS AND COMBUSTION MODIFICATIONS APPLIED FOR OIL AND GAS AS OF APRIL 1981 (TOKYO ELECTRIC)

| Methods of Combustion Modification                      | Number of Boilers | Total Generating Output (MW) |
|---------------------------------------------------------|-------------------|------------------------------|
| FGR <sup>a</sup> only                                   | 15                | 1,857                        |
| FGR + Two stage combustion                              | 12                | 5,289                        |
| FGR + Low NO <sub>x</sub> burner                        | 9                 | 2,710                        |
| FGR + Two stage combustion + Low NO <sub>x</sub> burner | <u>32</u>         | <u>13,605</u>                |
| Total                                                   | 68                | 23,461                       |

<sup>a</sup>Flue Gas Recirculation

TABLE 2-2. NO<sub>x</sub> ABATEMENT BY COMBUSTION MODIFICATION (CM) FOR UTILITY BOILERS

|                             | GAS     | OIL     | COAL    |
|-----------------------------|---------|---------|---------|
| NO Control                  | 200-300 | 250-350 | 500-800 |
| GM <sup>a</sup>             | 150-200 | 180-250 | 400-600 |
| TSC <sup>b</sup>            | 150-250 | 180-250 | 300-500 |
| GM + TSC                    | 100-150 | 120-200 | 250-400 |
| GM + TSC + LNB <sup>c</sup> | 50-90   | 80-140  | 150-300 |

<sup>a</sup>Gas Mixing (Flue Gas Recirculation)

<sup>b</sup>Two-Stage Combustion

<sup>c</sup>Low-NO<sub>x</sub> Burner

Combustion modification has also been applied extensively in the U.S. and European countries. Combustion modification technology is similar in most of these countries. This section describes combustion modification with emphasis on low-NO<sub>x</sub> burners developed and used in Japan.

In addition, an advanced combustion modification process has been developed which reduces about 50% of the NO<sub>x</sub> emissions by injecting about 10% of the fuel above the flame followed by air addition to assure complete combustion. The process is also considered to be a flue gas treatment process and is described in Section 6.4.

### 2.1.2 NO<sub>x</sub> from Pulverized Coal Burning

The reduction of NO<sub>x</sub> in flue gas from pulverized coal combustion has become very important in Japan because of the rapid increase in coal consumption and high NO<sub>x</sub> concentrations in the combustion gas. Reduction of fuel NO<sub>x</sub> is of particular importance because coal contains much larger amounts of nitrogen (1-3%) than does oil (0.1-0.5%). The fuel NO<sub>x</sub> from coal consists of volatile NO<sub>x</sub> derived from volatile nitrogen compounds in the coal and char NO<sub>x</sub> derived from residual nitrogen compounds in the char. Abatement of the volatile NO<sub>x</sub> can be accomplished efficiently by combustion control. Char NO<sub>x</sub> control may not be accomplished as easily since it is less sensitive to injection design modifications in the early stage of combustion.

Staged combustion is highly effective for NO<sub>x</sub> abatement for pulverized coal flue gas because it reduces both fuel and thermal NO<sub>x</sub>. On the other hand, flue gas recirculation (gas mixing) is less effective because it reduces thermal NO<sub>x</sub> which is not as much of a problem for coal-burning facilities.

Various types of low-NO<sub>x</sub> burners have been developed and used in combination with other combustion modification techniques such as staged combustion and flue gas recirculation as shown in Table 2-3.

TABLE 2-3. EXAMPLES OF COMBUSTION MODIFICATION FOR COAL-FIRED UTILITY BOILERS

| Station<br>(Company)        | Boiler<br>(MW)   | Coal<br>Source | Burner Type                       | NO <sub>x</sub> (ppm) |
|-----------------------------|------------------|----------------|-----------------------------------|-----------------------|
| ISOGO (EPDC)                | 265 <sup>a</sup> | Domestic       | DF-CN <sup>c</sup>                | 150-200               |
| Tomato-Atsuma<br>(Hokkaido) | 350 <sup>b</sup> | Domestic       | Dual Air <sub>d</sub><br>Register | 200                   |
| Matsushima (EPDC)           | 500 <sup>b</sup> | Imported       | SGR <sup>e</sup>                  | 200-280               |

<sup>a</sup> Staged combustion is used.

<sup>b</sup> Staged combustion and flue gas recirculation are used.

<sup>c</sup> See Section 2.2.

<sup>d</sup> See Section 2.3.

<sup>e</sup> See Section 2.4.

## 2.2 NO<sub>x</sub> ABATEMENT BY IHI-FW DF-CN COAL BURNER (1, 2, 3)

### 2.2.1 IHI-FW DF-CN Burner

Ishikawajima-Harima Heavy Industries (IHI) and Foster Wheeler Corporation of the U. S. have developed a low-NO<sub>x</sub> burner called the IHI-FW DF-CN (Dual Flow Convergent Fuel Nozzle) burner. It is based on the following principles for NO<sub>x</sub> reduction:

- 1) Minimum primary/secondary mixing prior to completion of the combustion of volatile fraction.
- 2) Ignition stability at the injector.
- 3) Dilution of the secondary air with recirculating combustion products.

The configuration of the burner is shown in Figure 2-1. The secondary air sharing the largest portion of total combustion air is divided into an outer and inner flow by an annular flow divider located between the outer sleeve of the coal nozzle and throat ring. The flow quantity and/or the swirl intensity of inner air is controlled by changing the opening of the circularly-linked inner vane located just downstream of the secondary air vane. The inner swirled air is supplied mainly to the burner axis zone, where the fuel-rich combustion of volatile matter takes place and stabilizes the flame. The outer swirled air is supplied along the periphery of the burner throat and controls the mixing with char particles as well as strengthening the external recirculation flow of combustion products.

The pulverized fuel is injected through a ring-shaped convergent nozzle, so that fuel-rich combustion on the burner axis can take place. The inner sleeve of the fuel nozzle can be moved toward and away from the furnace. The velocity of the injected fuel may be varied to some extent by moving the inner sleeve, and thus the initial mixing of fuel and air may be controlled.

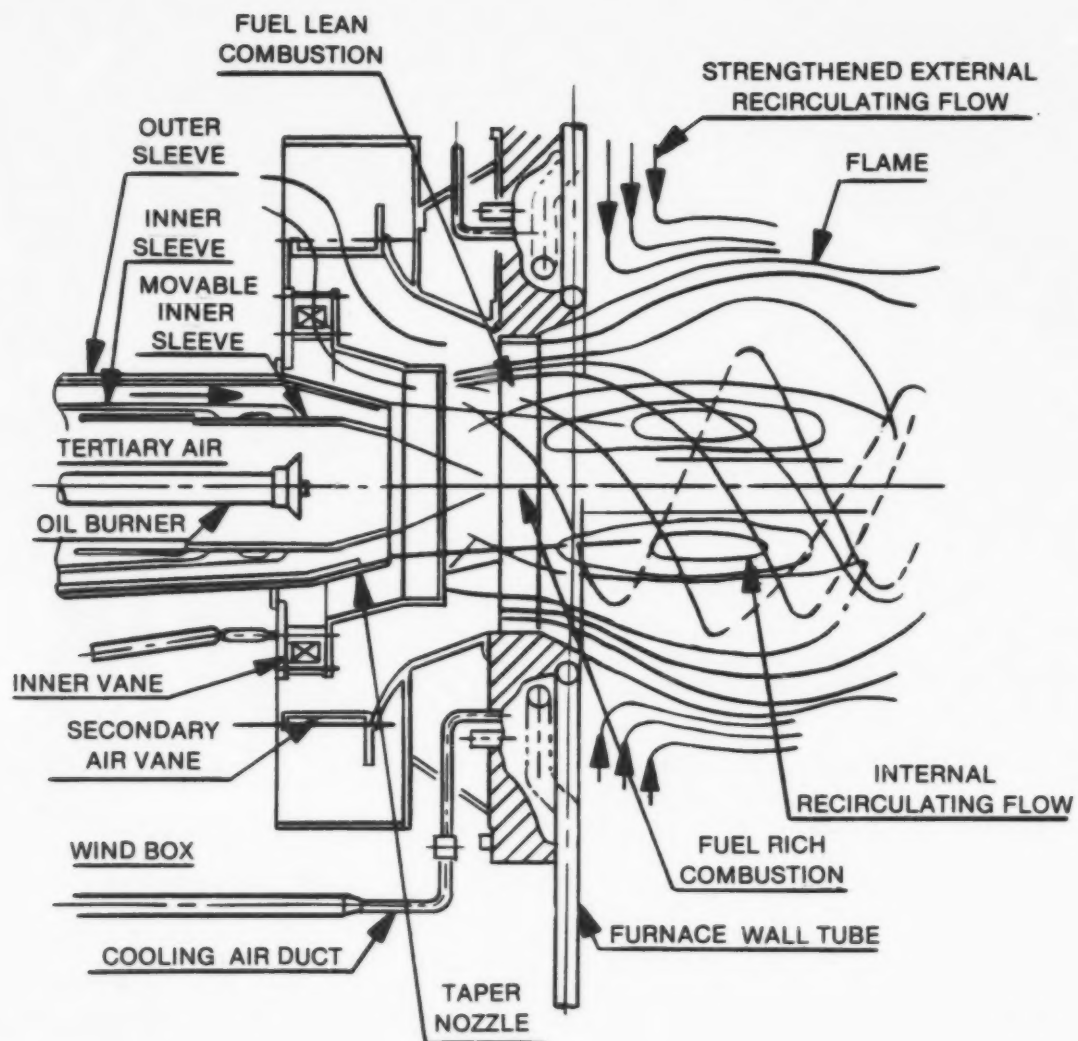


Figure 2-1 DF-CN Burner.



### 2.2.2 Test Furnace and Coal Composition

IHI conducted a combustion test using DF-CN type burners with a capacity of 2,000 kg/hr on a test furnace installed at IHI's Aioi Works. The study consisted of two stages. During the first stage, the characteristics of the DF-CN burner were investigated. During the second stage, other combustion modifications such as staged combustion and/or flue gas recirculation were examined for use with the DF-CN burner. The test furnace is illustrated in Figure 2-2. It was designed to have a geometrical similarity to the actual furnace of the coal-fired boiler. Single-burner and overfire-air ports (OAP) for staged combustion were installed on the front wall. Maximum heat input to the furnace is approximately  $11 \times 10^6$  kcal/hr. Secondary air is preheated by a tubular gas-air heater to a wind box air temperature of almost 300°C.

The compositions of the coals used for these tests are shown in Table 2-4.

### 2.2.3 Test Results

The results of tests conducted with Japanese coal A are shown in Figures 2-3 through 2-6. The  $O_2$  concentration in the flue gas was about 4%.

Figure 2-3 shows that  $NO_x$  decreases as the swirl intensity of secondary air is reduced by the opening of the secondary air vane. Figure 2-4 shows that  $NO_x$  decreases sharply when the opening of the inner vane is reduced; it reaches a minimum before the vane is entirely closed. Figure 2-5 indicates that the tertiary air stream has a strong effect on  $NO_x$ . The increase in fuel injection velocity assisted by tertiary air is assumed to be the cause of the decrease in  $NO_x$  emissions.

The primary air/coal ratio and the position of the inner sleeve influence  $NO_x$  emissions by changing the fuel injection velocity. The effect of the injection velocity on  $NO_x$  removal is shown in Figure 2-6.

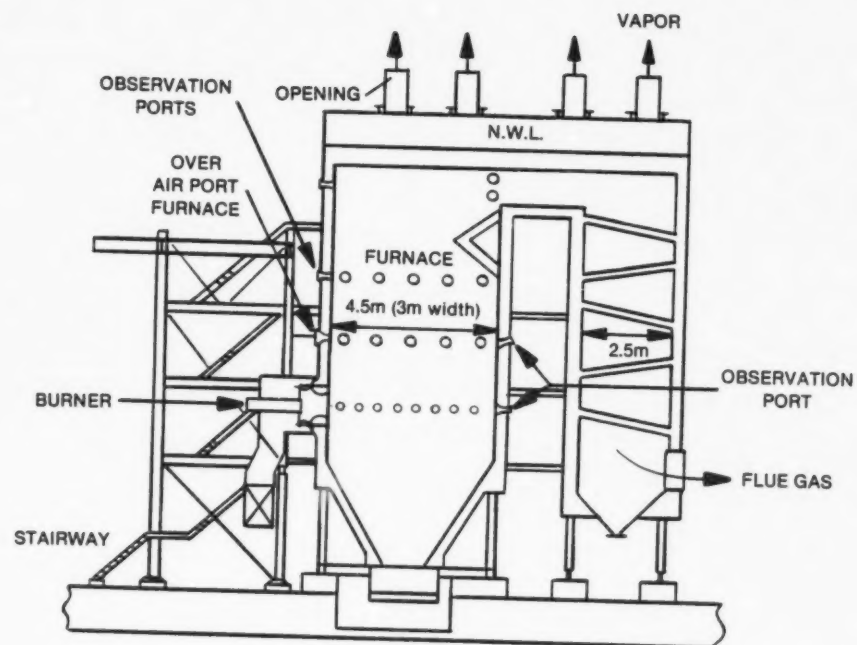


Figure 2-2 Cross-section View of Test Furnace.

TABLE 2-4. COMPOSITIONS OF COALS TESTED

| Kind of Coal                      | Japanese Coal |       |       | Imported Coal |       |       |       |
|-----------------------------------|---------------|-------|-------|---------------|-------|-------|-------|
|                                   | A             | B     | C     | A             | B     | C     | D     |
| <u>Proximate Analysis</u>         |               |       |       |               |       |       |       |
| Higher Heating Value<br>(kcal/kg) | 6,200         | 6,600 | 5,410 | 6,870         | 7,220 | 6,740 | 6,460 |
| Inherent Moisture, %              | 5.29          | 1.61  | 1.72  | 3.72          | 4.06  | 3.13  | 4.53  |
| Volatile Matter, %                | 43.9          | 39.1  | 35.8  | 28.7          | 41.4  | 34.6  | 32.5  |
| Ash, %                            | 13.9          | 18.4  | 31.1  | 10.4          | 5.44  | 12.7  | 12.8  |
| Fixed Carbon, %                   | 36.9          | 40.9  | 31.3  | 57.2          | 49.1  | 49.6  | 50.2  |
| <u>Ultimate Analysis</u>          |               |       |       |               |       |       |       |
| C, %                              | 62.9          | 66.6  | 52.7  | 72.8          | 71.8  | 68.0  | 65.2  |
| H, %                              | 5.1           | 5.0   | 4.4   | 4.1           | 5.0   | 4.3   | 4.1   |
| N, %                              | 1.1           | 0.9   | 0.7   | 1.0           | 1.4   | 1.4   | 2.3   |
| S, %                              | 0.26          | 2.31  | 1.37  | 0.81          | 0.43  | 0.60  | 0.98  |
| O, %                              | 10.66         | 4.84  | 7.45  | 6.74          | 11.62 | 9.44  | 9.43  |

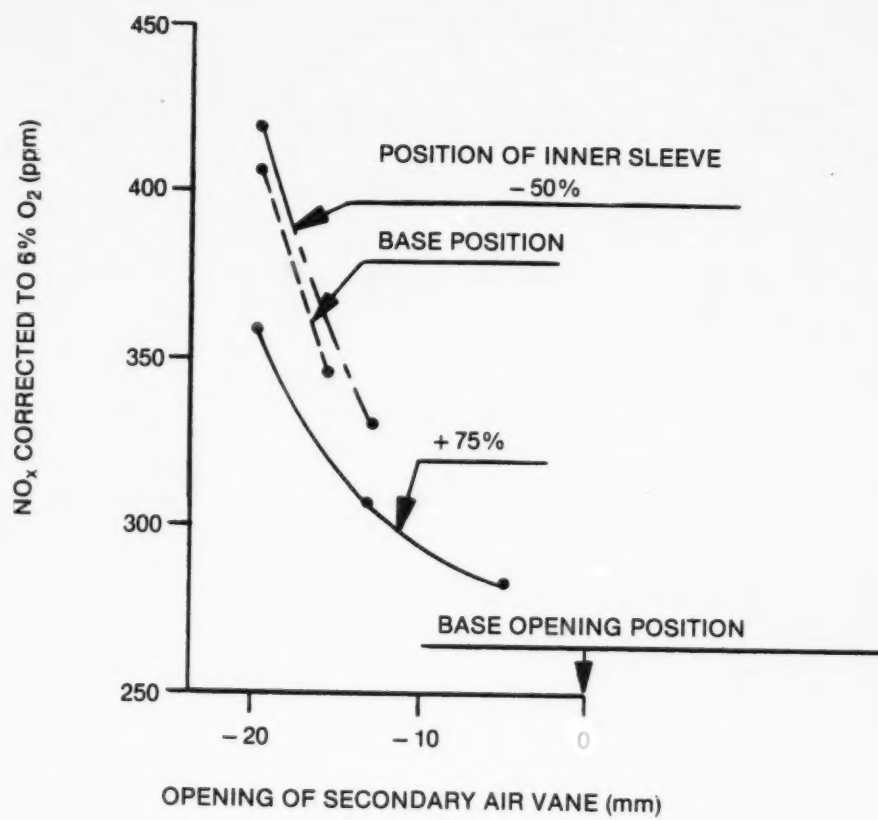


Figure 2-3 Secondary Air Vane Opening vs. No<sub>x</sub>.

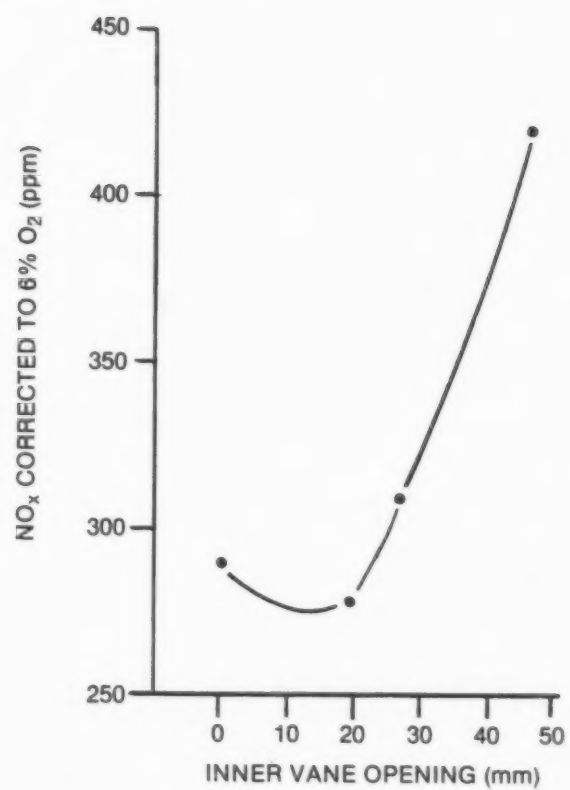


Figure 2-4 Inner Vane Opening vs. NO<sub>x</sub>.



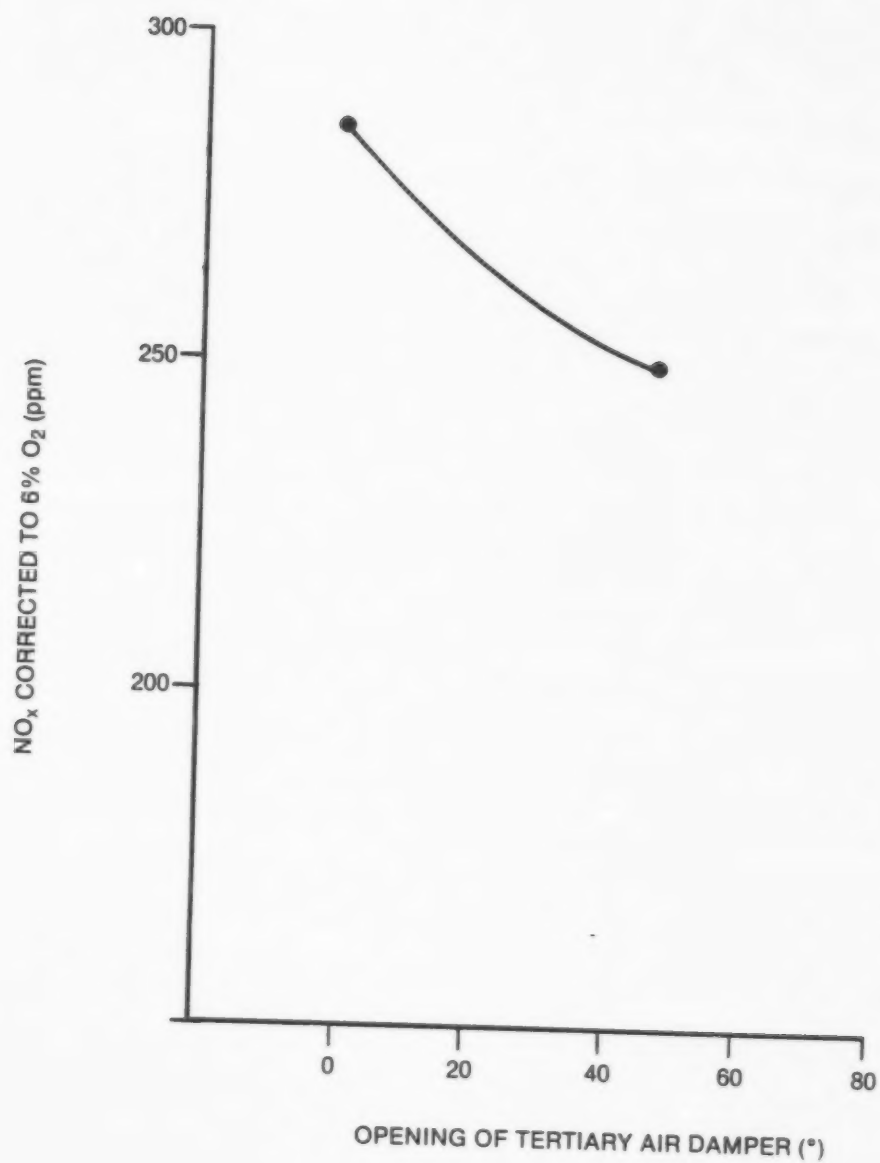


Figure 2-5 Opening of Tertiary Air Damper vs. NO<sub>x</sub>.

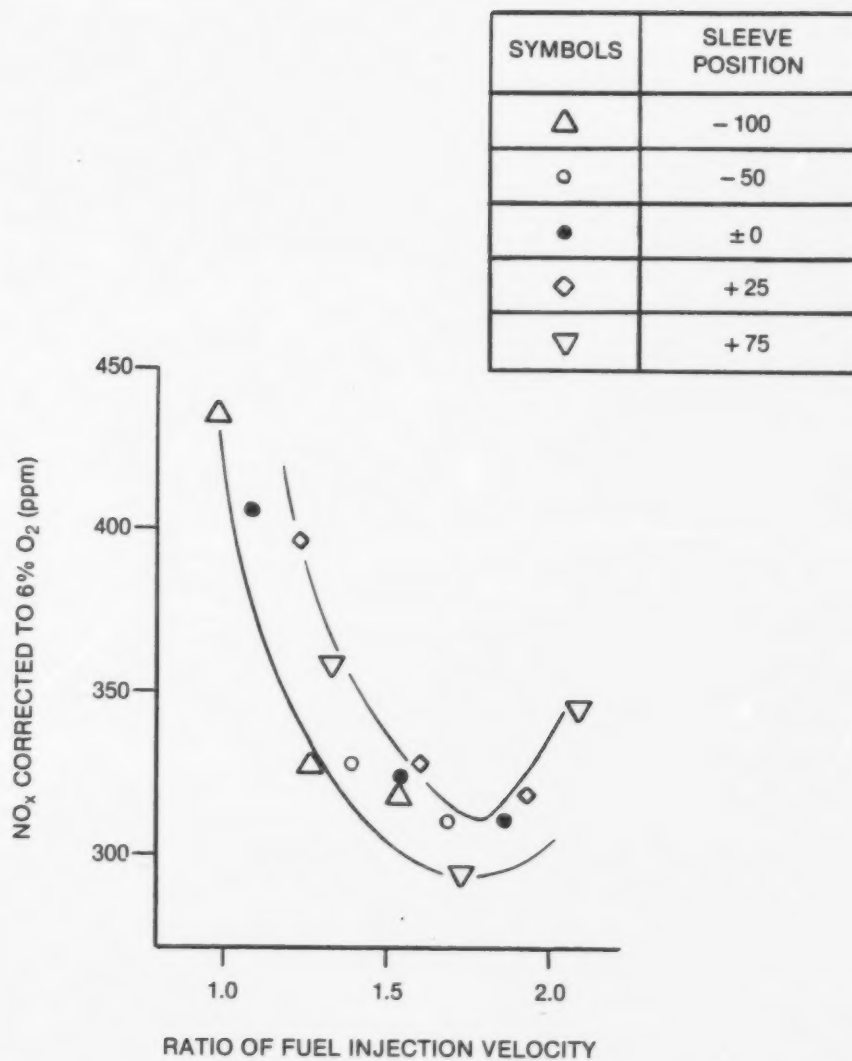


Figure 2-6 Effect of Fuel Injection Velocity on NO<sub>x</sub>.

The effects of staged combustion and flue gas recirculation on the performance of the low- $\text{NO}_x$  burner were also studied. Three over-fire air ports were installed—one of them straight above the burner and the others on either side of the air port. Figure 2-7 shows that  $\text{NO}_x$  was reduced substantially by lowering the burner stoichiometry; it reached about 150 ppm at 0.8 stoichiometry. The relationship between the nitrogen content of the coal and the  $\text{NO}_x$  concentration at different burner stoichiometries is shown in Figure 2-8. By using a lower stoichiometry, most of the fuel  $\text{NO}_x$  can be reduced to  $\text{N}_2$  which reduces  $\text{NO}_x$  to a low level even with a high-nitrogen coal. Figure 2-9 shows the effect of flue gas recirculation on  $\text{NO}_x$  concentration. By using the combination of a low- $\text{NO}_x$  burner, staged combustion, and flue gas recirculation,  $\text{NO}_x$  was reduced to about 100 ppm, even with high-nitrogen coal.

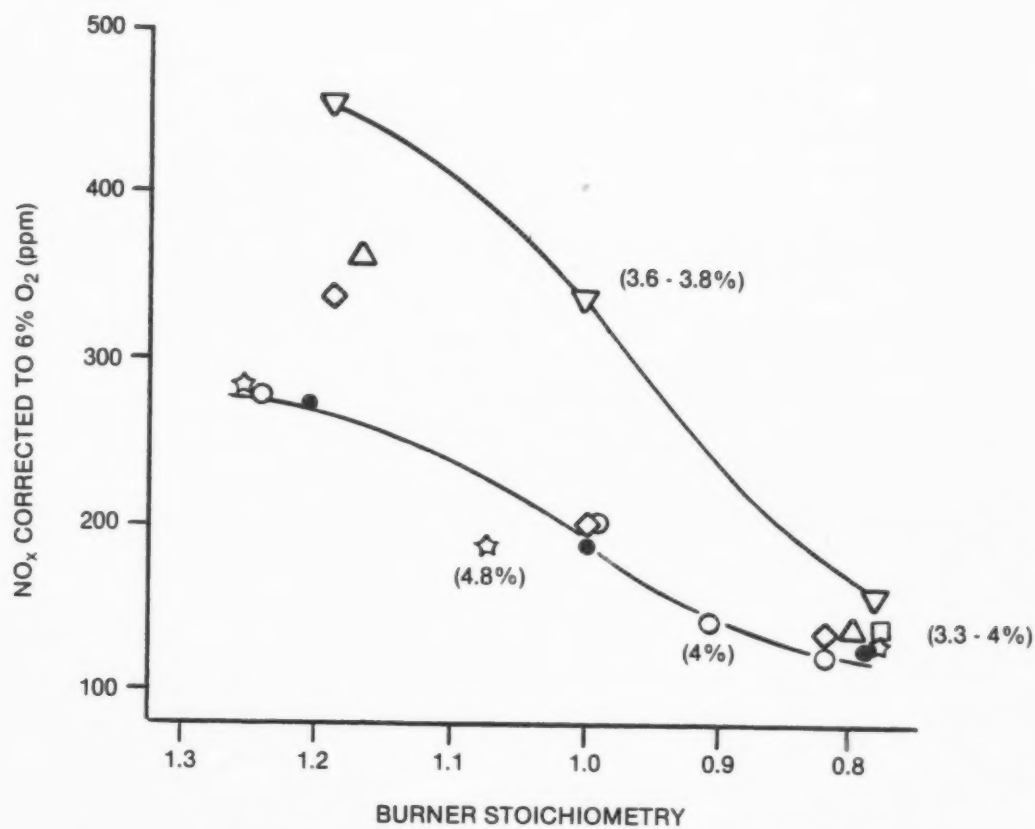
Commercial application of the burner is described in Section 2.6.3.

### 2.3 $\text{NO}_x$ ABATEMENT BY BHK LOW- $\text{NO}_x$ COAL BURNER (4,5,6)

#### 2.3.1 Primary Gas Dual Air Register Burner

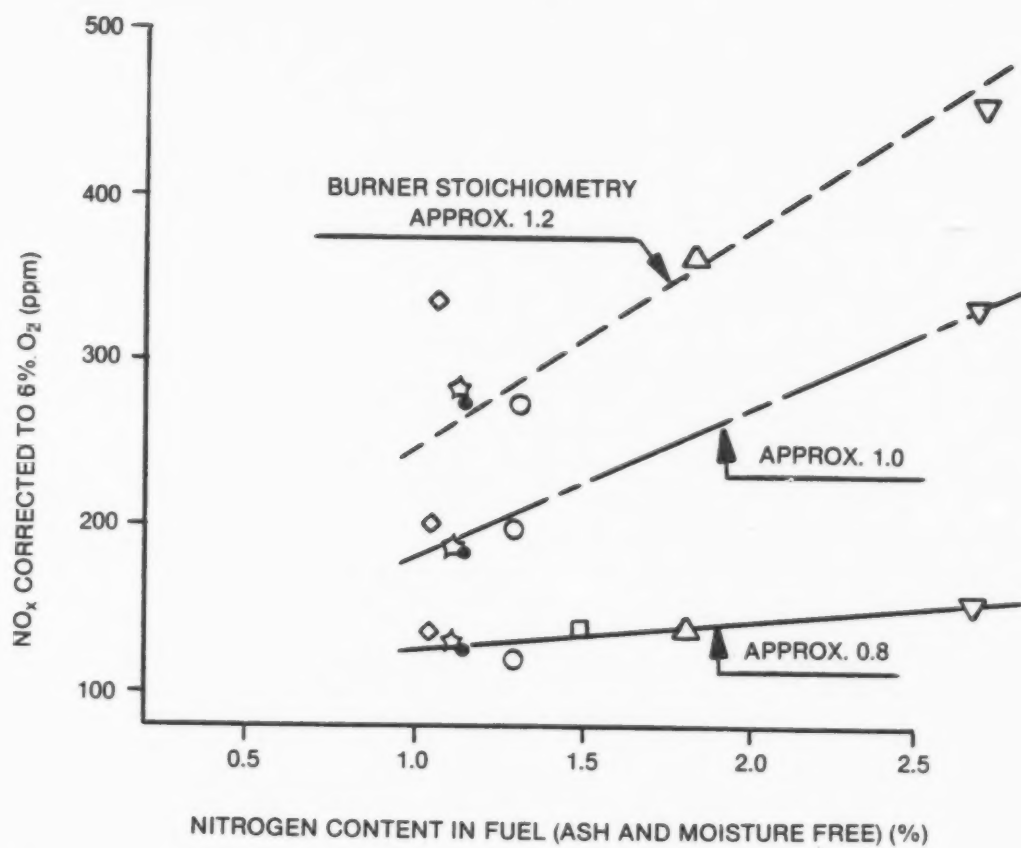
This low- $\text{NO}_x$  burner is based on the dual air register burner developed by Babcock and Wilcox of the U.S. with an improvement made by Babcock-Hitachi K.K. (BHK). The major difference between this burner and the dual air register burner is that the former has a primary gas (PG) port for injection of recirculated flue gas to reduce  $\text{NO}_x$  formation. Figure 2-10 shows the construction of the burner. The nozzle for pulverized coal is located in the center of the air register and allows injection of pulverized coal which is mixed with air (primary air) and sent into the furnace. The pulverized coal injection nozzle has two concentric cylindrical sleeves. The inner of the cylindrical paths formed by them is called the primary gas port and the outer is called the secondary air port. The cylindrical path formed by the outer sleeve of the secondary air port and the burner throat is called the tertiary air port.

|   |               |   |
|---|---------------|---|
| ○ | JAPANESE COAL | A |
| ☆ |               | B |
| ◇ |               | C |
| ● | IMPORTED COAL | A |
| □ |               | B |
| △ |               | C |
| ▽ |               | D |



NOTE: Figures in Parentheses indicate Exhaust Gas O<sub>2</sub>.

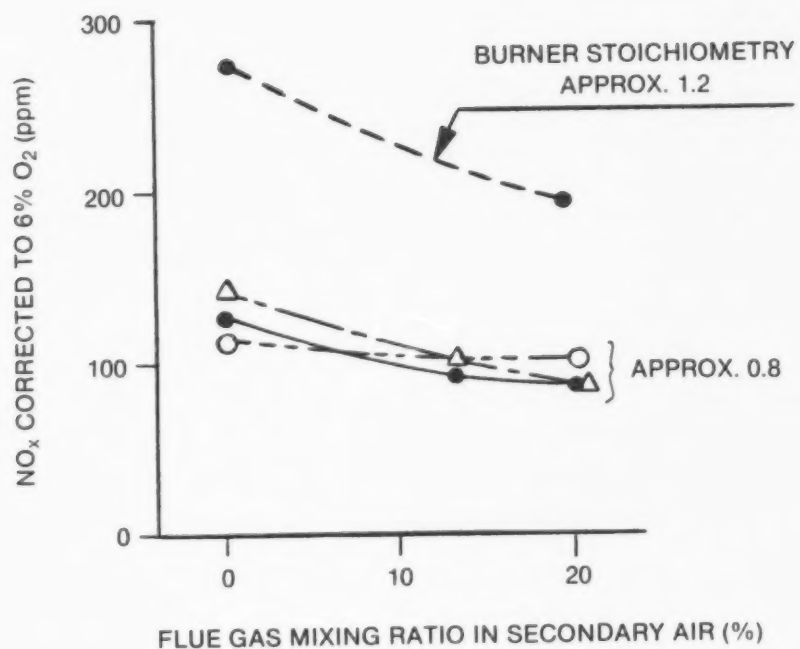
Figure 2-7 NO<sub>x</sub> Reduction by Low-NO<sub>x</sub> Burner and Two-staged Combustion.



NOTE: Symbols in This Figure are the same as those in Figure 2-7.

Figure 2-8 Nitrogen Content in Fuel vs. NO<sub>x</sub>.





NOTE: Symbols in this Figure are the same as those in Figure 2-7.

Figure 2-9 NO<sub>x</sub> Reduction by Flue Gas Recirculation.

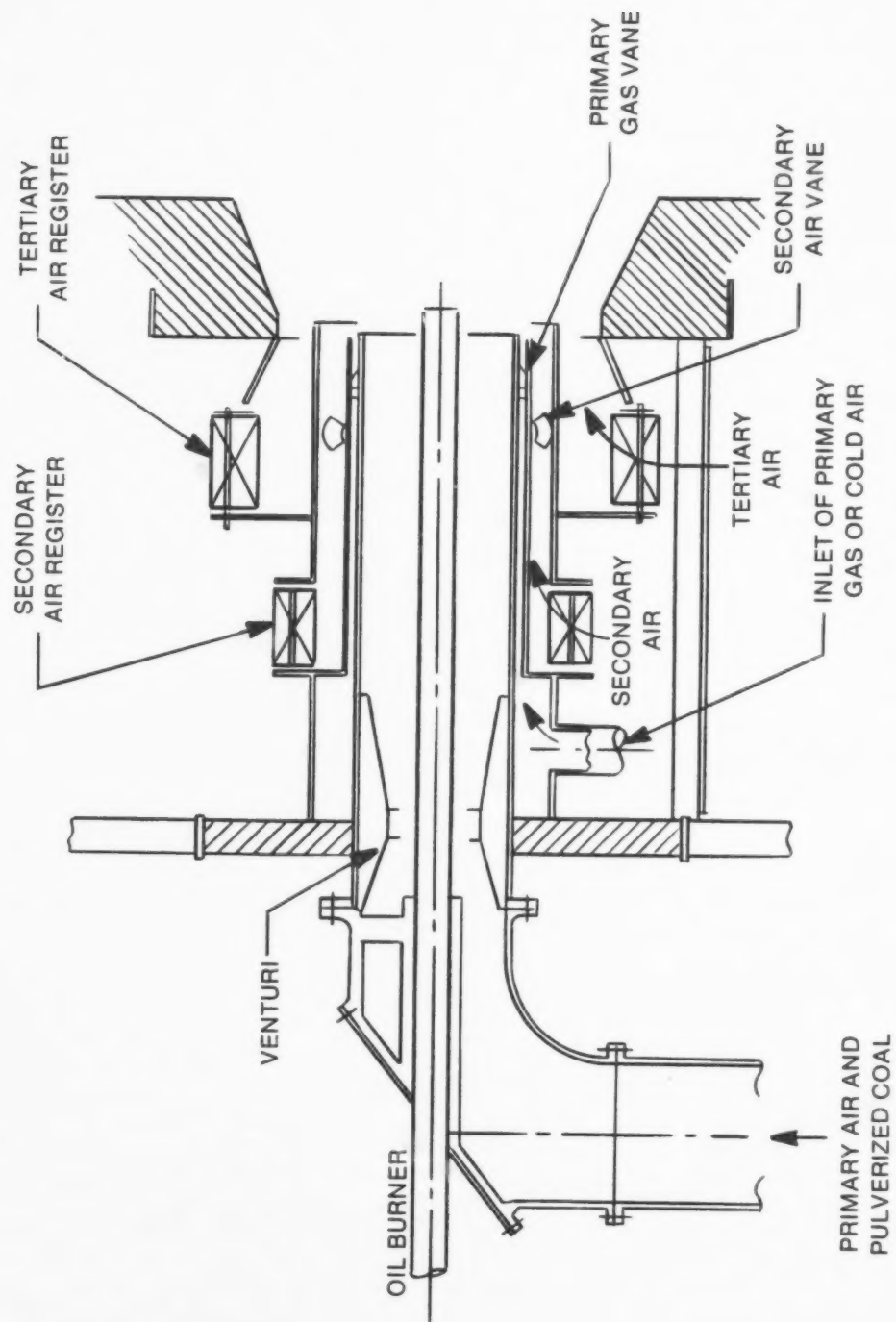


Figure 2-10 PG Dual-Air Register Burner.

Combustion air from the windbox is supplied to the secondary and tertiary air ports. Each port is equipped at its inlet with louvre dampers, called secondary and tertiary registers, for distributing the air flow among these ports. Each of the nozzles accommodates a specific amount of combustion air. In addition, the PG type burner uses a primary gas port to introduce flue gas from the economizer outlet and slow the rapid mixing of the fuel-rich flame with secondary air.

### 2.3.2 Test Results

Results of tests with a 250 MW natural circulation coal-fired boiler are shown in Figure 2-11. The A portion of the figure shows the relationship between the two-stage combustion ratio (air through the burner throat/theoretical air) and the  $\text{NO}_x$  concentrations for a conventional circular burner and the PG dual air register burner. Assuming that the  $\text{NO}_x$  concentration with the conventional burner without two-stage combustion is 100%, the reduction ratio was 31% with two-stage combustion, 39% with the use of the PG dual air register burner, and 63% with the combination of two-stage combustion and the PG burner.

Figure 2-11 B gives an example of the relationship between CO concentration and the two-stage combustion ratio. CO emissions increased up to the two-stage combustion ratio of 87 and then decreased. The variation in two-stage combustion ratios causes variation in the flow ratios of the secondary and tertiary air. Because of this variation the injection speed of the combustion air at the burner throat also varies. On the other hand, the relative speed between the air side and fuel side at the burner throat varies because the fuel injection speed (primary air) is constant. The concentration of CO seems to increase at zero relative speed.

Figures 2-12 and 2-13 show the effects of  $\text{O}_2$  levels in flue gas and boiler loads on  $\text{NO}_x$  emission levels. Figure 2-14 illustrates the results of using different coals in a test furnace as shown in Table 2-5. The application of primary gas along with staged combustion and flue gas recirculation

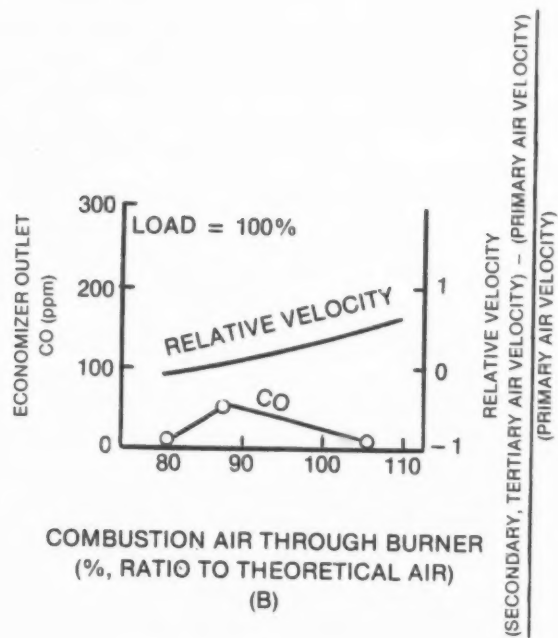
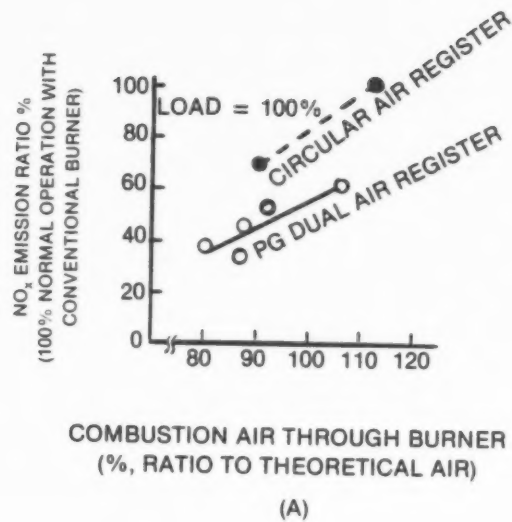


Figure 2-11 Results of Two-Staged Combustion Test: NO<sub>x</sub> and CO.

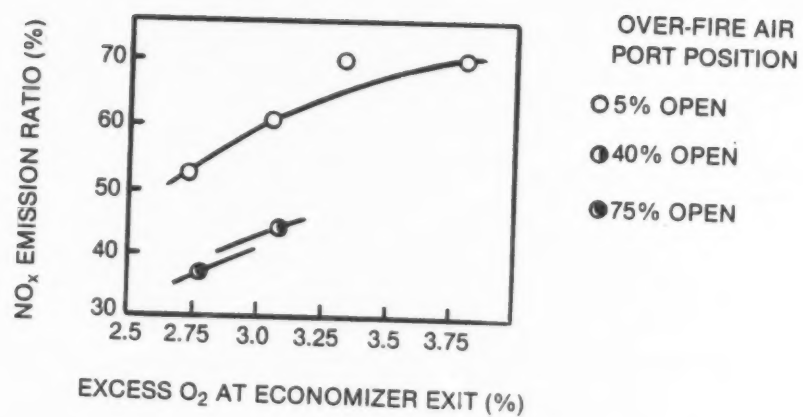


Figure 2-12 Effect of Flue Gas O<sub>2</sub> Level on NO<sub>x</sub> Emissions in PG Dual Register Burner.

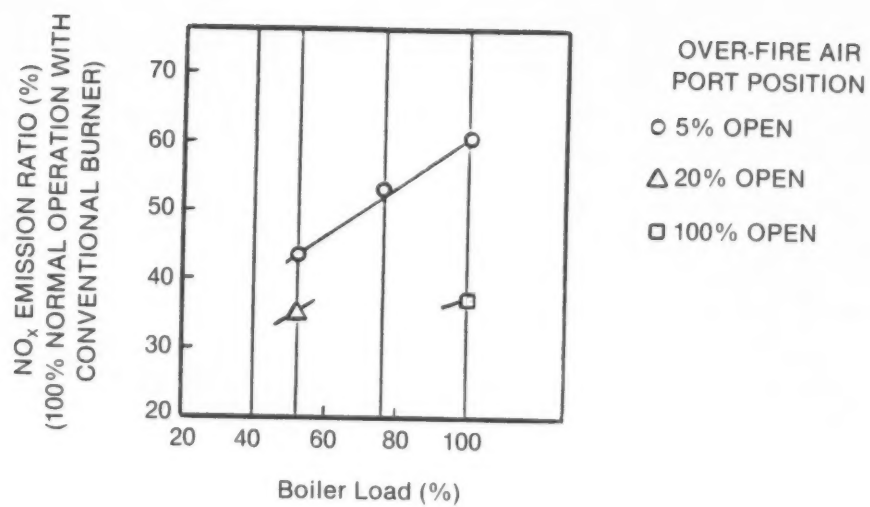


**Figure 2-13** Effect of Boiler Load on NO<sub>x</sub> Emissions in PG Dual Register Burner.



| BURNER TYPE          | COAL       | NO OTHER CONTROL | 2 STAGE COMBUSTION | 2 STAGE + GM | 2 STAGE + GM + PG |
|----------------------|------------|------------------|--------------------|--------------|-------------------|
| DUAL AIR REGISTER    | JAPANESE   | X                |                    |              |                   |
| PG DUAL AIR REGISTER | JAPANESE   | ○                | ●                  | ●            | ●                 |
|                      | OVERSEAS A | △                | ▲                  | ▲            | ▲                 |
|                      | OVERSEAS B | □                | ■                  | ■            | ■                 |

2 STAGE COMBUSTION: 85% BURNER STOICHIOMETRY

GM = GAS MIXING (FLUE GAS RECIRCULATION)

PG = FLUE GAS (6.5%) FED THROUGH THE BURNER

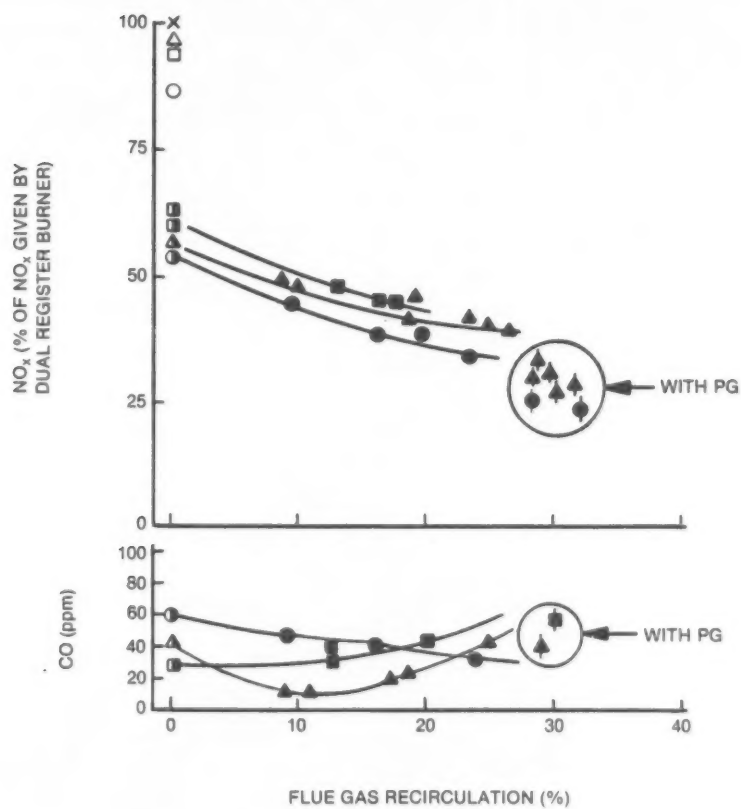


Figure 2-14 Performance of the PG Dual Register Burner in the Test Furnace.

TABLE 2-5. COMBUSTION FURNACE TEST CONDITIONS FOR FACTORY TEST

1. Furnace  
 Type: Horizontal water-cooled cylinder  
 Size: Inner diameter 2.2m  
       Length 9.0m  
 Combustion capacity:  
       max.  $13 \times 10^6$  kcal/h
2. Type of burner  
 (1) Dual air register  
 (2) P.G. Dual air register
3. Type of coal  
 (1) Japanese coal: 1,000 kg/h  
 (2) Overseas coal A: 930 kg/h  
 (3) Overseas coal B: 870 kg/h
4. Air temperature: 300°C
5. Furnace outlet O<sub>2</sub>: 3.0%
6. Fuel analysis:

| Type of Coal | Japanese Coal | Overseas Coal |   |
|--------------|---------------|---------------|---|
|              |               | A             | B |

Proximate Analysis

|                 |         |       |       |       |
|-----------------|---------|-------|-------|-------|
| GCV (Dry Base)  | kcal/kg | 6,040 | 6,494 | 6,900 |
| Moisture        | %       | 1.90  | 2.04  | 2.60  |
| Volatile matter | %       | 32.29 | 25.64 | 28.20 |
| Fixed carbon    | %       | 40.91 | 55.74 | 57.30 |
| Ash             | %       | 24.90 | 16.58 | 12.00 |

Ultimate Analysis

|              |     |       |       |       |
|--------------|-----|-------|-------|-------|
| Total sulfur | %   | 1.0   | 0.83  | 0.70  |
| Carbon       | %   | 59.86 | 67.76 | 71.98 |
| Hydrogen     | %   | 4.08  | 3.53  | 4.12  |
| Nitrogen     | %   | 1.09  | 1.61  | 0.90  |
| Oxygen       | %   | 8.07  | 8.41  | 10.02 |
| Sulfur       | %   | 0.64  | 0.53  | 0.42  |
| Fluorine     | ppm | 106   | 1,581 | —     |

reduced  $\text{NO}_x$  to about 25% of the level obtained with conventional combustion. CO was not increased by using primary gas.

The performance of the PG-type burner will be discussed in Section 2.6 (Figure 2-35).

#### 2.4 MHI LOW- $\text{NO}_x$ COAL BURNERS (7,8,9)

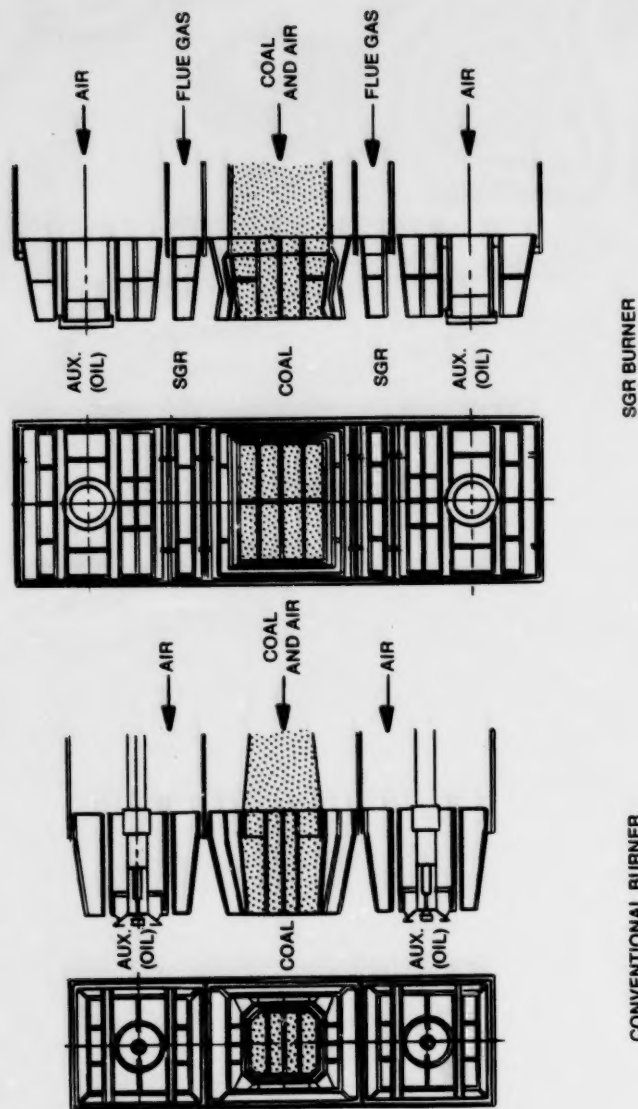
##### 2.4.1 Separate Gas Recirculation Burner

Mitsubishi Heavy Industries (MHI) developed a low- $\text{NO}_x$  separate gas recirculation (SGR) burner, which is used with the new 500 MW coal-fired boiler at EPDC's Matsushima Station. Recently MHI further improved the SGR burner to produce a PM coal burner.

By conducting extensive fundamental studies, MHI has found the following conditions to be important for  $\text{NO}_x$  abatement.

- 1) The temperature in the volatile matter combustion zone should be kept as high as possible and the combustibles should stay in this zone as long as practicable.
- 2) The temperature of the char combustion zone should be appropriately low and combustion should be completed in this zone.

Figure 2-15 compares the SGR burner with a conventional burner. The SGR burner has several features to satisfy the conditions described above. A flame holder is provided at the outlet of the coal nozzle to maintain a stable ignition and expedite the combustion of volatile matter. The coal nozzle and each auxiliary air nozzle are located apart from one another and SGR nozzles are placed between them to retard the diffusion of secondary air to the volatile matter combustion zone.



(Oil Burners are for Start-up)

**Figure 2-15** Configurations of Conventional and SGR Burners.

Extensive combustion tests have been carried out with a test furnace shown in Figure 2-16 and described in Table 2-6, using coals shown in Table 2-7. As shown in Figure 2-17,  $\text{NO}_x$  concentrations were 30-50% lower with the SGR burner than with a conventional burner.  $\text{NO}_x$  abatement was more pronounced with the Japanese coal which had a low fixed carbon (FC)/volatile matter (VM) ratio. As will be shown in Figure 2-24, data obtained with the test furnace agree well with the data from commercial boilers.

#### 2.4.2 PM Burner for Pulverized Coal

Figure 2-18 indicates that the  $\text{NO}_x$  concentration falls as the primary air/coal ratio (kg/kg) decreases from 3 to 1. Figure 2-19 shows that the  $\text{NO}_x$  concentration is also lowered when the ratio increases from 3 to 7.

As shown in Figure 2-20, a ratio of 3~4 approximately corresponds to the theoretical air for volatile matter in coal.  $\text{NO}_x$  concentrations are lowered with the smaller ratio because of the deficiency of  $\text{O}_2$ . On the other hand, the ratio 7~8 corresponds to the theoretical air for coal. With the ratio of between 3~4 and 7~8, fixed carbon in coal burns with deficient  $\text{O}_2$  to form  $\text{NO}_x$ .

A conventional burner may produce a primary air/coal ratio of 2~3 as shown in Figure 2-20. If the primary air-coal supply is divided into two streams with different ratios— $C_1$  for a coal-rich concentrated nozzle and  $C_2$  for coal-lean weak nozzle—for separate burning, the average  $\text{NO}_x$  value should be  $(\text{NO}_x)\text{PM}$  as shown in the figure. This is the weighted mean of  $(\text{NO}_x)C_1$  and  $(\text{NO}_x)C_2$  and is substantially lower than  $(\text{NO}_x)C_0$ . The combined use of the concentrated flame and weak flame may result in low- $\text{NO}_x$  combustion.

Figure 2-21 shows the configuration of the Pollution Minimum (PM) burner for use with coal. The performance of the PM burner in the test furnace is shown in Figures 2-22 and 2-23. A low  $\text{NO}_x$  concentration, about 100 ppm or below, was achieved by the furnace.

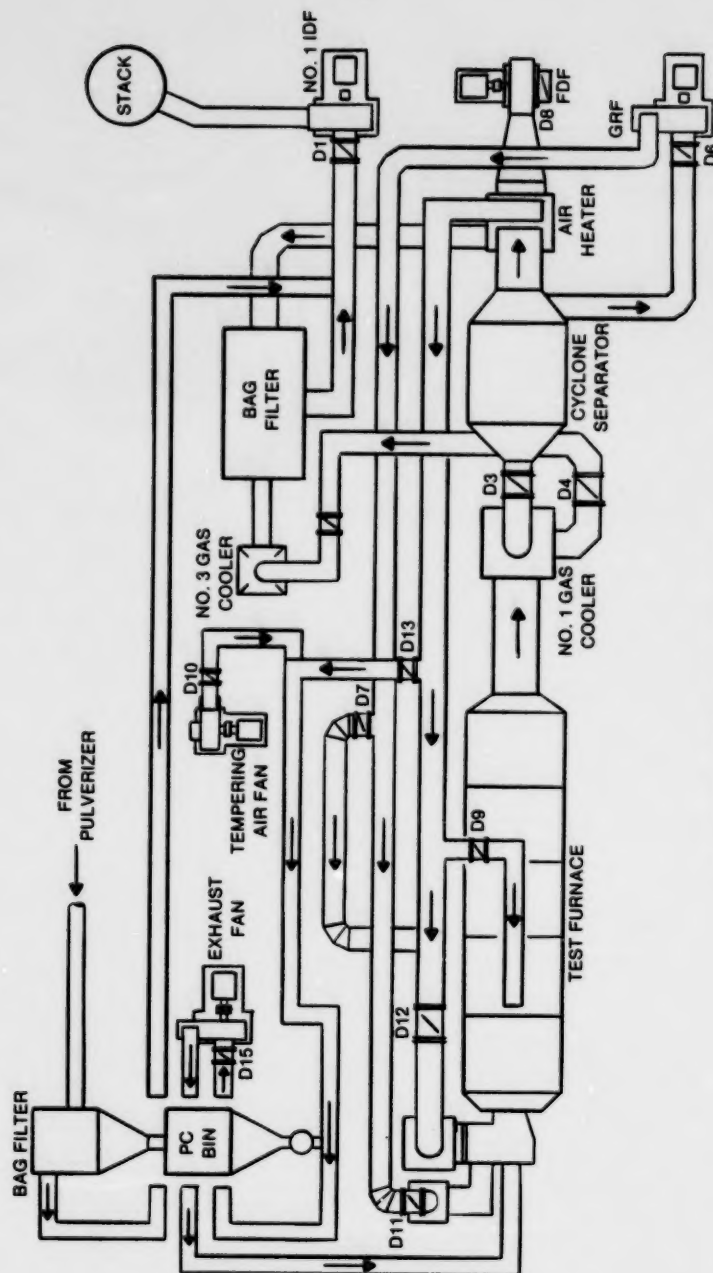


Figure 2-16 Flowsheet of the 40/hr Test Furnace.

70A2601



TABLE 2-6. MAIN FEATURES OF MHI TEST FURNACE (4 t/hr Test Furnace)

| Equipment          | Technical details                                                                                   |
|--------------------|-----------------------------------------------------------------------------------------------------|
| Test furnace       | Horizontally installed, water cooled, circular-walled steel construction. 4.4 diameter, 20 m length |
| F.D. fan           | Capacity: 920m <sup>3</sup> /min x 800mmAq at 20°C, Motor: 160kw                                    |
| No. 1 I.D. fan     | Capacity: 1140m <sup>3</sup> /min x 800mmAq at 100°C, Motor: 330kw                                  |
| Fan                | No. 2 I.D. fan Capacity: 200m <sup>3</sup> /min x 320mmAq at 100°C, Motor: 30 kw                    |
| Exhaust fan        | Capacity: 260m <sup>3</sup> /min x 700mmAq at 100°C, Motor: 90kw                                    |
| G.R. fan           | Capacity: 760m <sup>3</sup> /min x 600 mmAq at 350°C, Motor: 165kw                                  |
| Air Heater         | Ljungstrom type, Capacity: 750Nm <sup>3</sup> /min x (25 350°C)                                     |
| Gas                | No. 1 Gas cooler Water-cooled tubular type, Capacity: 750nm <sup>3</sup> /min x (800 500°C)         |
| Cooler             | No. 2 Gas cooler Water-cooled tubular type, Capacity: 200nm <sup>3</sup> /min x (700 120°C)         |
|                    | No. 3 Gas cooler Water cooled tubular type, Capacity: 100nm <sup>3</sup> /min x (700 350°C)         |
| Ash disposal       | Cyclone separator Multi-cyclone type, Capacity: 1000nm <sup>3</sup> /min x 500°C                    |
|                    | Bag filter Gas area 613m <sup>2</sup> , Capacity: 1200nm <sup>3</sup> /min x 120°C                  |
|                    | Precipitator Gas velocity: 1~1.5m/s, Capacity: 2500nm <sup>3</sup> /h                               |
| Fuel feed assembly | Coal pulverizer Bowl mill type, Capacity: 2300hg/h x 8000m <sup>3</sup> /h x 600mmAg                |
| P.C. bin           | Capacity: 20m <sup>3</sup>                                                                          |
| P.C. feeder        | Table feeder type, Capacity: Max 4500kg/h                                                           |

TABLE 2-7. ANALYSIS OF COALS USED WITH MHI TEST BURNER

| Coals         | Marks | Proximate analysis<br>(surface moisture free) |                        |            |              | Ultimate Analysis<br>(dry base) |          |            |      | HHV<br>(surface moisture free)<br>kcal/kg |
|---------------|-------|-----------------------------------------------|------------------------|------------|--------------|---------------------------------|----------|------------|------|-------------------------------------------|
|               |       | Volatile<br>Matter<br>(%)                     | Fixed<br>Carbon<br>(%) | Ash<br>(%) | FC/VM<br>(-) | N<br>(%)                        | O<br>(%) | O/N<br>(-) |      |                                           |
| Japanese      | H     | 42.8                                          | 40.2                   | 11.2       | 0.94         | 1.1                             | 13.9     | 11.0       | 6390 |                                           |
|               | I     | 31.6                                          | 46.0                   | 20.5       | 1.46         | 1.0                             | 6.6      | 6.6        | 6450 |                                           |
|               | J     | 26.3                                          | 59.7                   | 7.5        | 2.27         | 1.7                             | 11.5     | 7.2        | 6710 |                                           |
| Australian    | K     | 35.7                                          | 50.6                   | 10.1       | 1.42         | 1.4                             | 11.0     | 7.86       | 6930 |                                           |
|               | L     | 28.6                                          | 50.6                   | 17.8       | 1.77         | 1.5                             | 8.1      | 5.40       | 6410 |                                           |
|               | M     | 34.6                                          | 52.6                   | 10.9       | 1.50         | 1.5                             | 8.3      | 5.53       | 7120 |                                           |
| Chinese       | N     | 30.8                                          | 54.1                   | 14.1       | 1.77         | 1.1                             | 5.8      | 5.3        | 6730 |                                           |
|               | O     | 27.4                                          | 60.6                   | 8.8        | 2.21         | 0.86                            | 9.8      | 10.2       | 7100 |                                           |
|               | P     | 25.2                                          | 56.1                   | 15.5       | 2.23         | 1.9                             | 8.4      | 4.42       | 6520 |                                           |
| South African | Q     | 33.9                                          | 49.4                   | 12.8       | 1.46         | 1.7                             | 10.9     | 6.41       | 6540 |                                           |
|               | R     | 24.1                                          | 57.6                   | 15.2       | 2.39         | 1.5                             | 8.1      | 6.95       | 6490 |                                           |
|               | S     | 23.7                                          | 57.9                   | 14.2       | 2.44         | 1.6                             | 9.3      | 7.05       | 6350 |                                           |
| U.S.          | T     | 36.9                                          | 47.0                   | 9.9        | 1.27         | 1.1                             | 13.4     | 12.2       | 6060 |                                           |

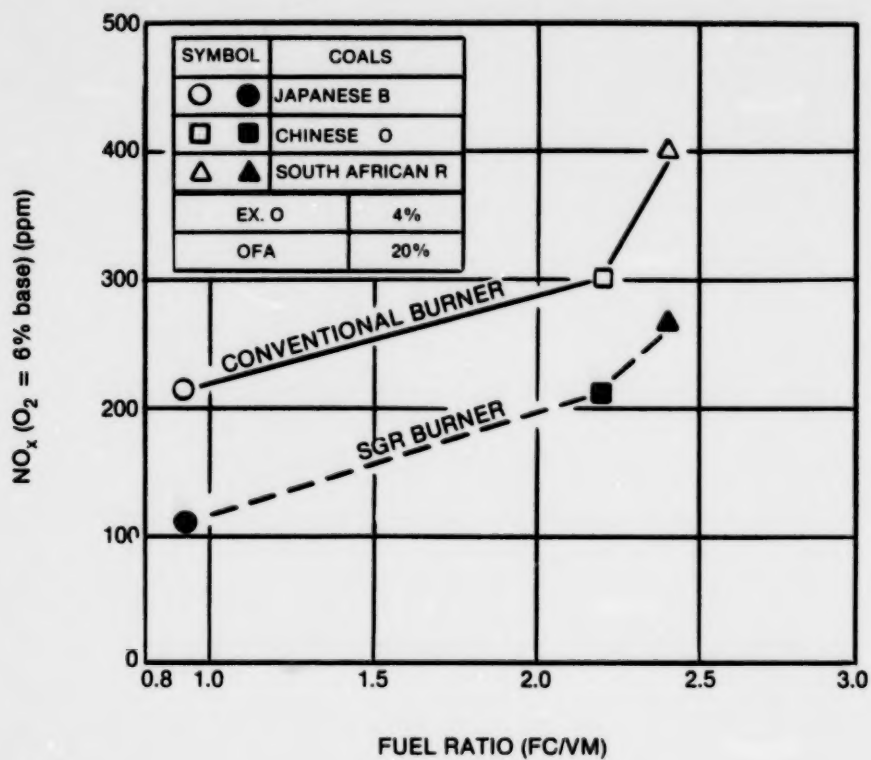


**Figure 2-17 Comparison of NO<sub>x</sub> Formation with SGR Burner and Conventional Burner.**

70A2602

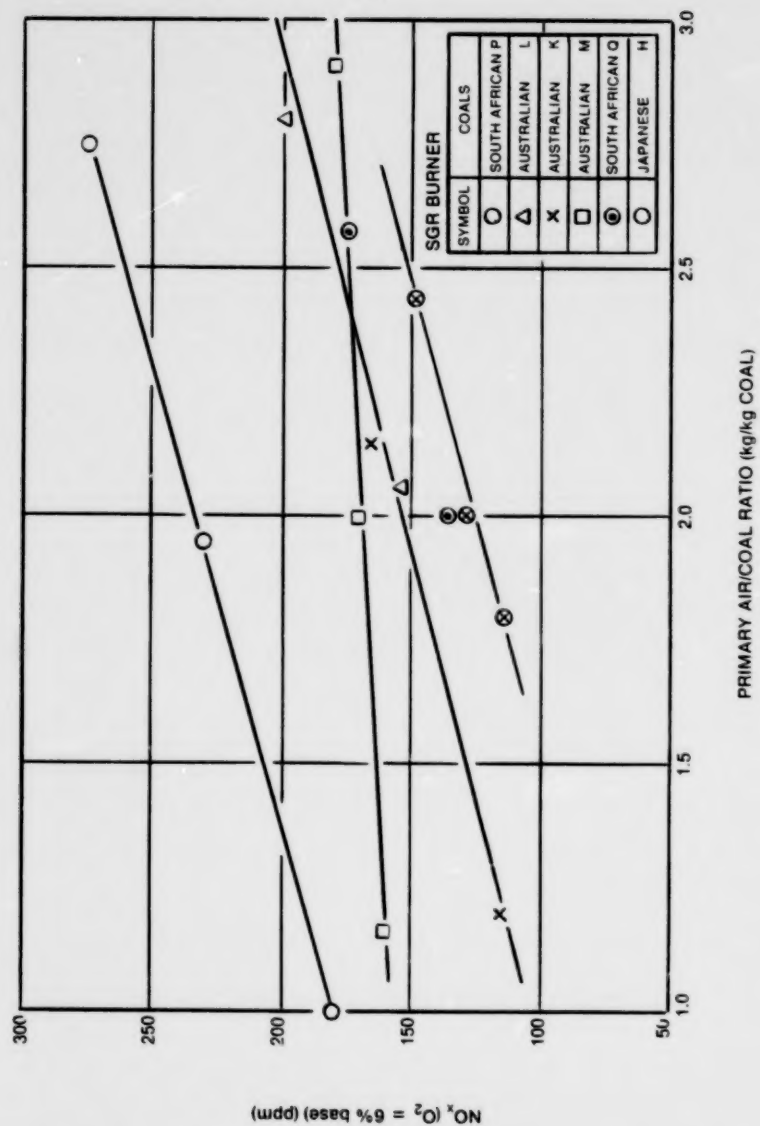


Figure 2-18 Effect of Primary Stage Stoichiometry on NO<sub>x</sub>. (Fuel-rich side)

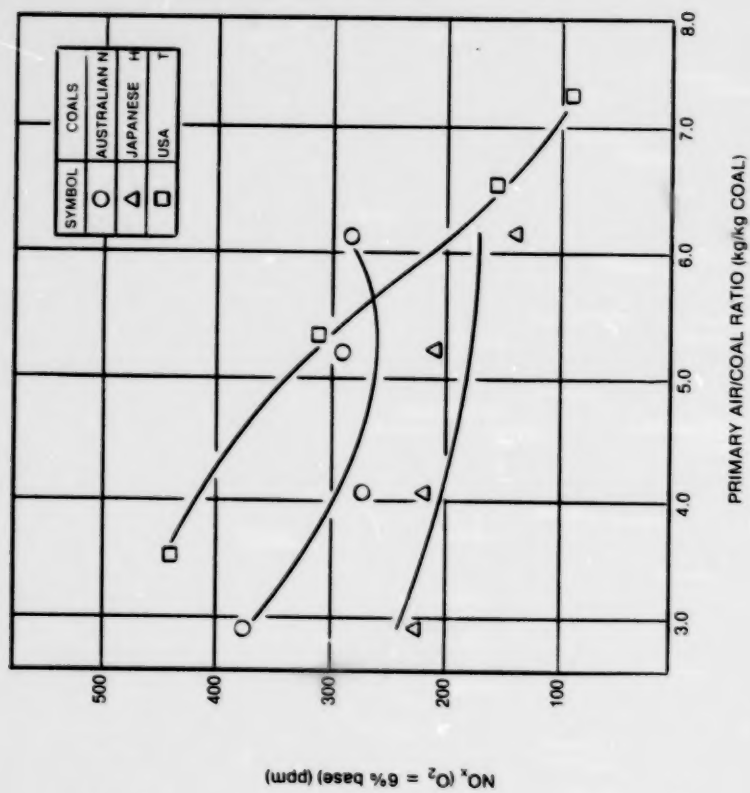


Figure 2-19 Effect of Primary Stage Stoichiometry on NO<sub>x</sub> (Fuel-lean side)

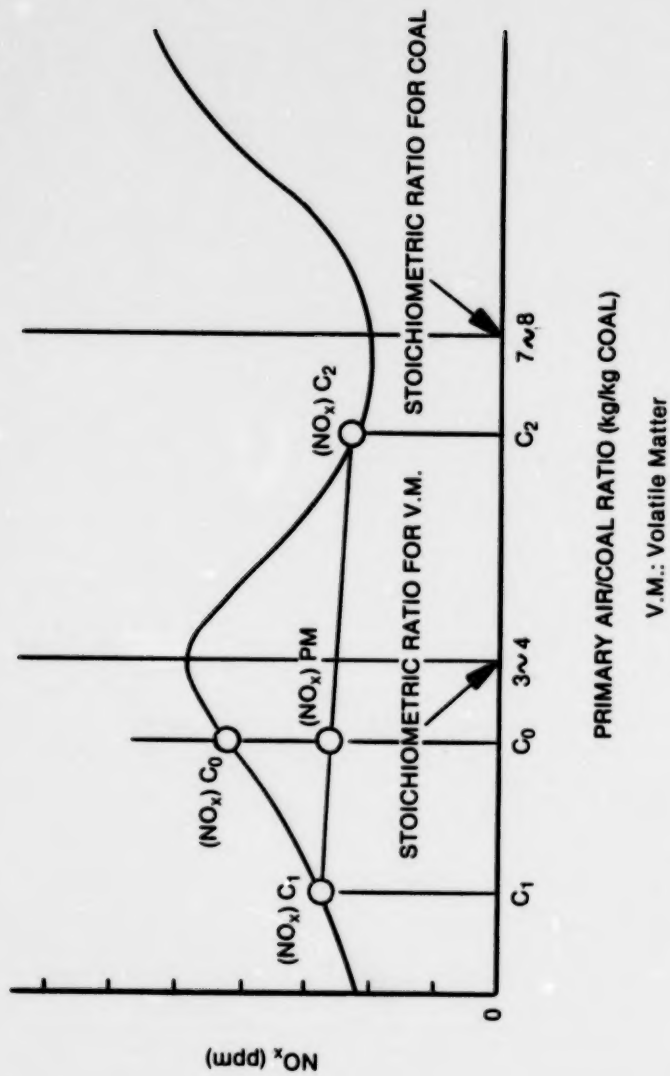


Figure 2-20 Concept of Pulverized Coal-fired Low  $\text{NO}_x$  PM Burner.

70A2605





Figure 2-21 Structure of the Coal-fired PM Burner.

| SYMBOL              | O<br>(CHINESE) | Δ<br>(JAPANESE) | □<br>P<br>(SOUTH AFRICAN) |
|---------------------|----------------|-----------------|---------------------------|
| COAL                |                |                 |                           |
| OFA %               | —              | —               | —                         |
| SGR %               | 0              | 0               | 0                         |
| GM %                | 0              | 0               | 0                         |
| EX O <sub>2</sub> % | 4.0            | 4.0             | 4.0                       |
| load %              | 100            | 100             | 100                       |

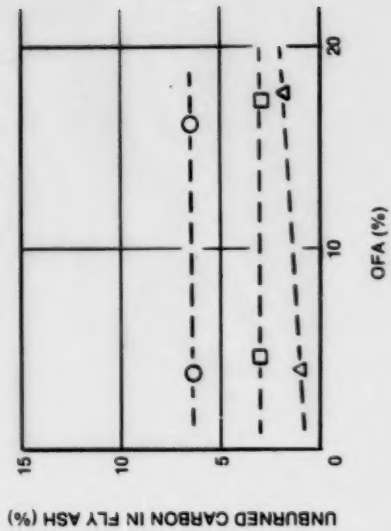
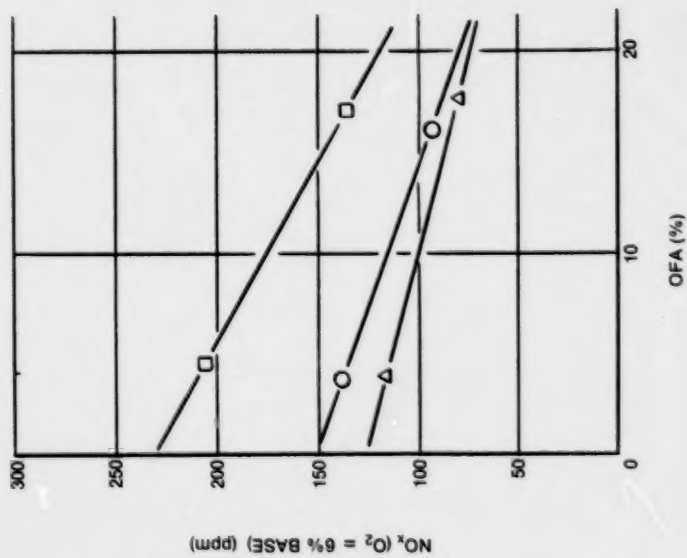


Figure 2-22 NO<sub>x</sub> and Unburned Carbon in Fly Ash vs. OFA. (PM Burner)

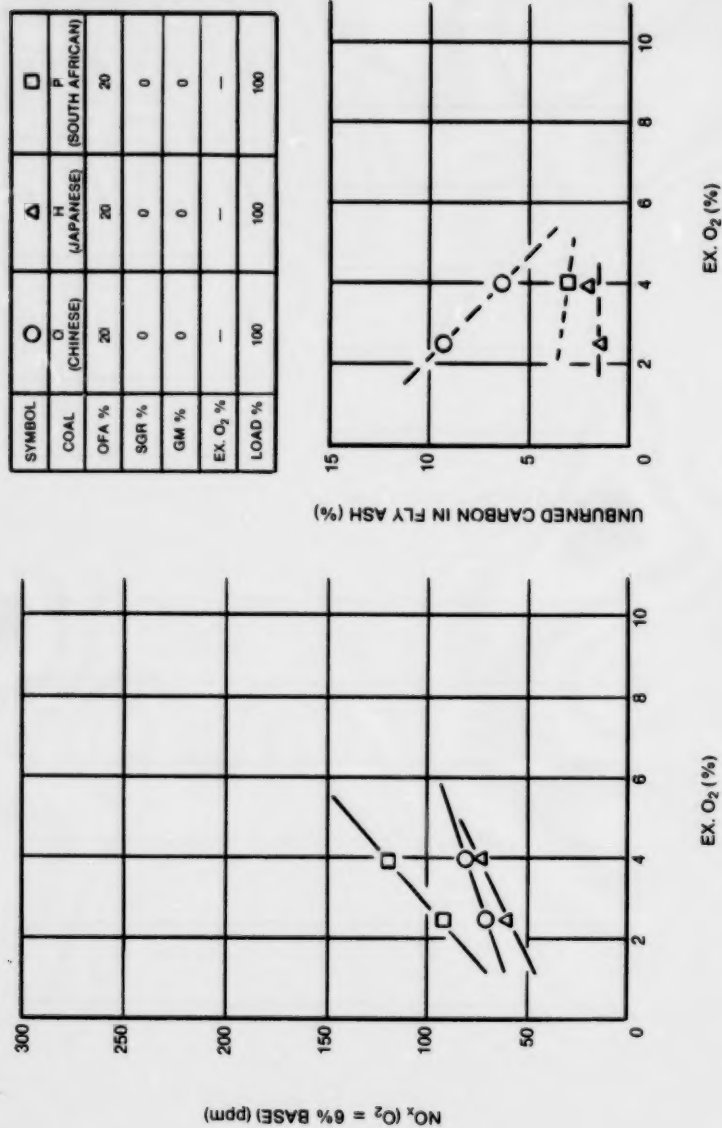
Figure 2-23 NO<sub>x</sub> and Unburned Carbon in Fly Ash vs. Ex.O<sub>2</sub> (PM Burner)

Figure 2-24 compares the  $\text{NO}_x$  concentrations for a Combustion Engineering (CE) conventional burner, SGR burner and PM burner when used for tangential-firing commercial boilers and the test furnace. Since  $\text{NO}_x$  concentrations for test boilers agree well with those for commercial boilers, it is expected that with use of a commercial PM burner,  $\text{NO}_x$  concentrations may be reduced to 60-80 ppm with Japanese coals and 100-150 ppm with imported coals.

## 2.5 KHI LOW- $\text{NO}_x$ COAL BURNER (11,12)

### 2.5.1 Structure and Combustion Model

Kawasaki Heavy Industries (KHI) initially developed a low- $\text{NO}_x$  coal burner for pulverized coal as shown in Figure 2-25. Later KHI improved the burner design and developed a vortex diffuse (VD) burner as shown in Figure 2-26.

KHI's burners are designed to reduce  $\text{NO}_x$  efficiently by using low- $\text{NO}_x$  burners in combination with staged combustion. The primary air is swirled intensely; much larger amounts of secondary and tertiary air are introduced to provide slow contacting with the coal and the partial combustion products.

A combustion model is shown in Figure 2-27. In the primary combustion zone (I of the figure), volatile matter begins to burn, producing high concentrations of  $\text{NO}_x$  due to the combustion of nitrogen compounds in the coal. In the secondary zone (II), the volatile matter continues to burn, the char begins to burn, and  $\text{O}_2$  concentrations decrease, producing a reducing atmosphere which causes the decomposition of the  $\text{NO}_x$  to  $\text{N}_2$ . The reducing atmosphere also exists in the tertiary zone (III), where the  $\text{NO}_x$  concentrations reach a minimum just before the over-fire air port for staged combustion. The CO concentration remains high.

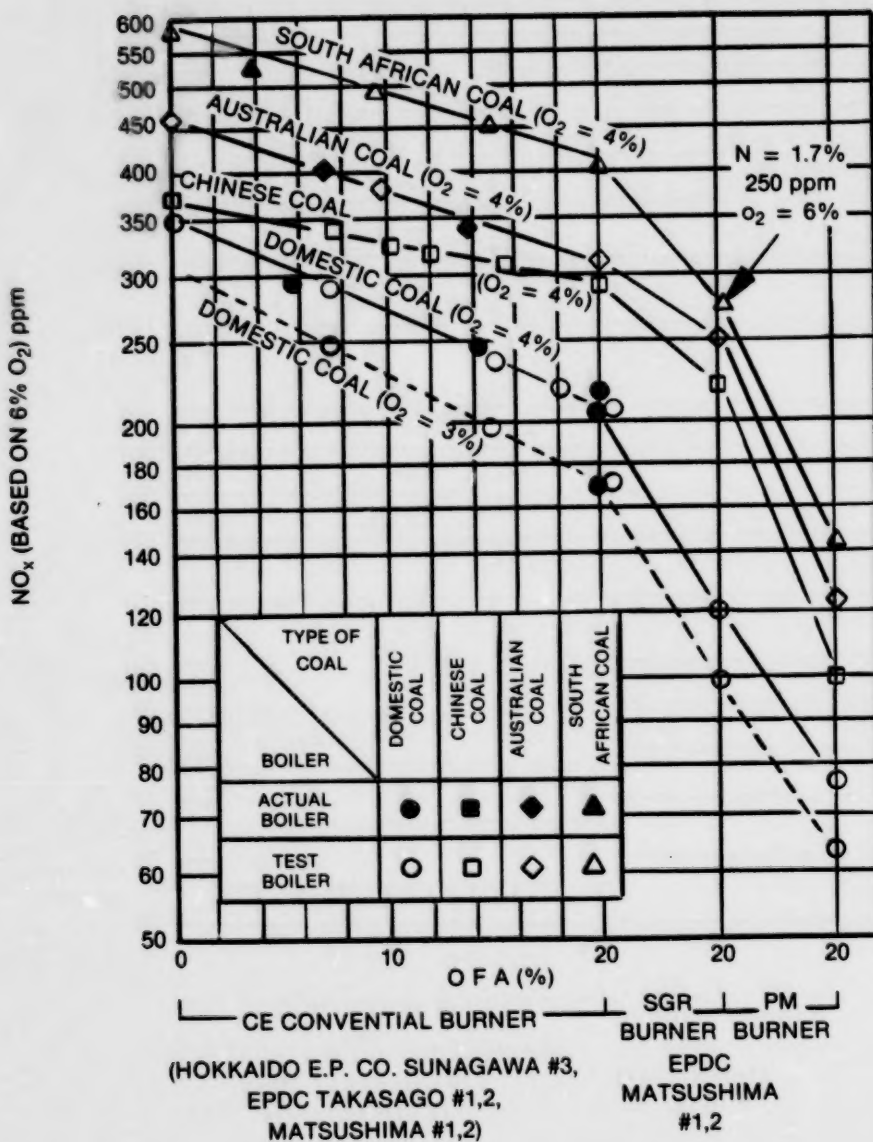


**Figure 2-24 Comparison of NO<sub>x</sub> Emissions: Laboratory Test Results vs. Field Data. (10)**

70A2609

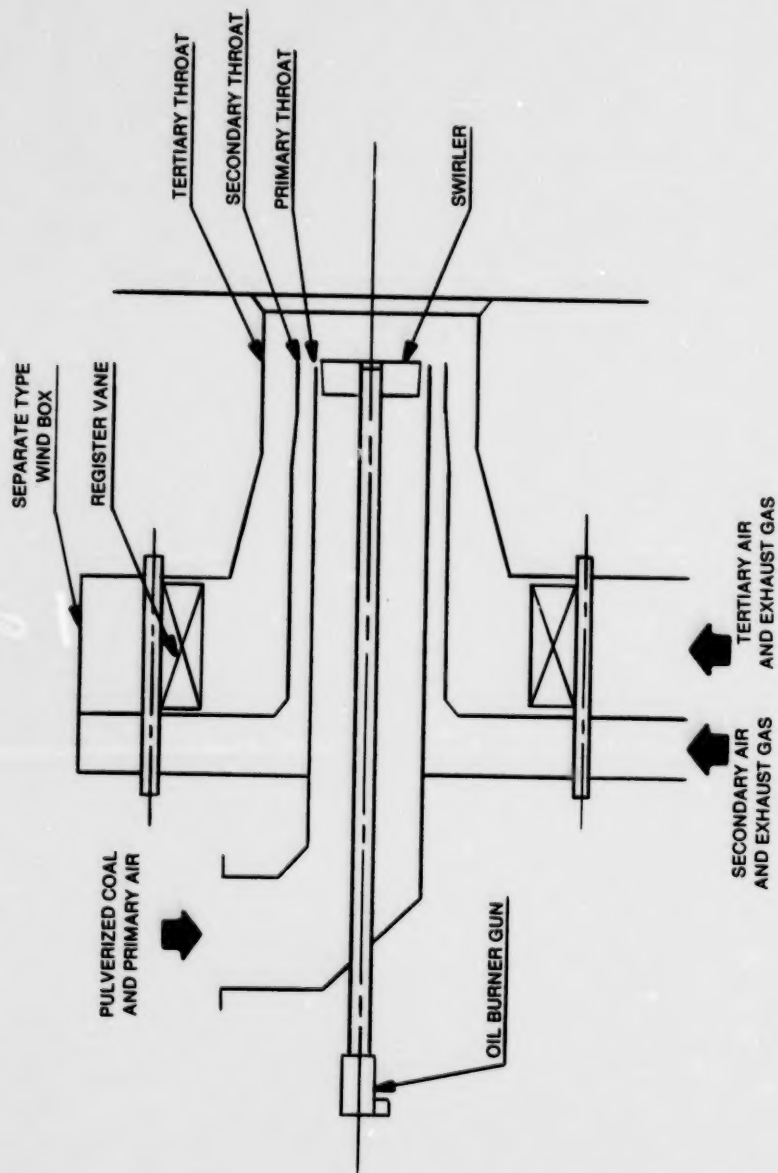


Figure 2.25 Structure of Original KHI Low-NO<sub>x</sub> Burner.



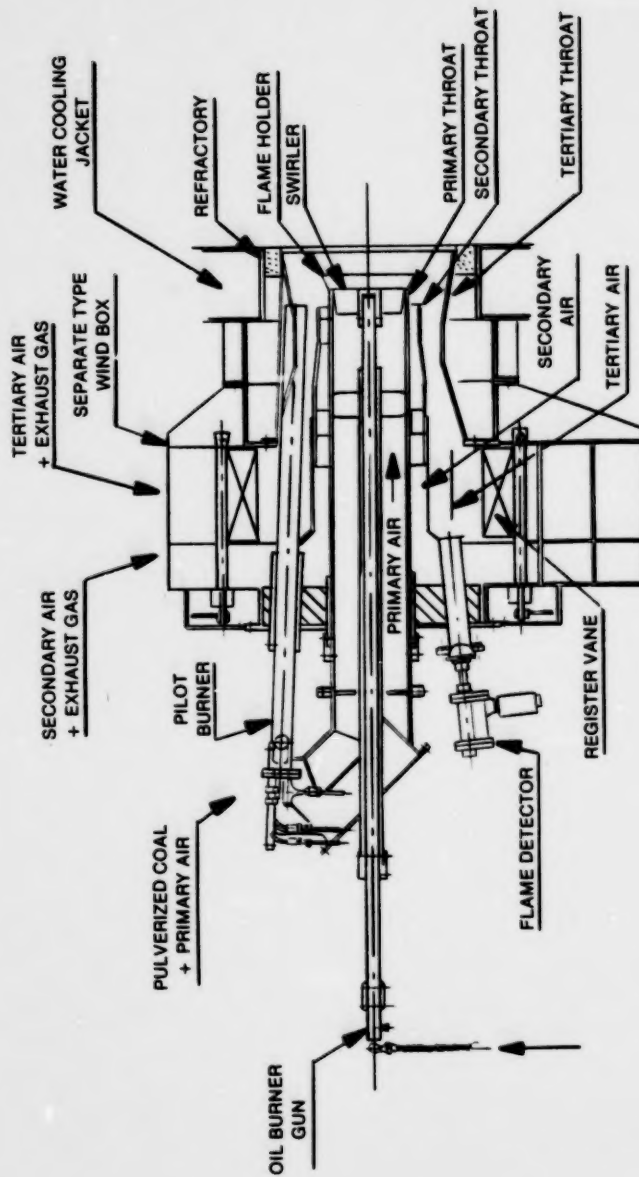


Figure 2-28 Structure of VD Low-NO<sub>x</sub> Pulverized Coal Burner.

70A2611

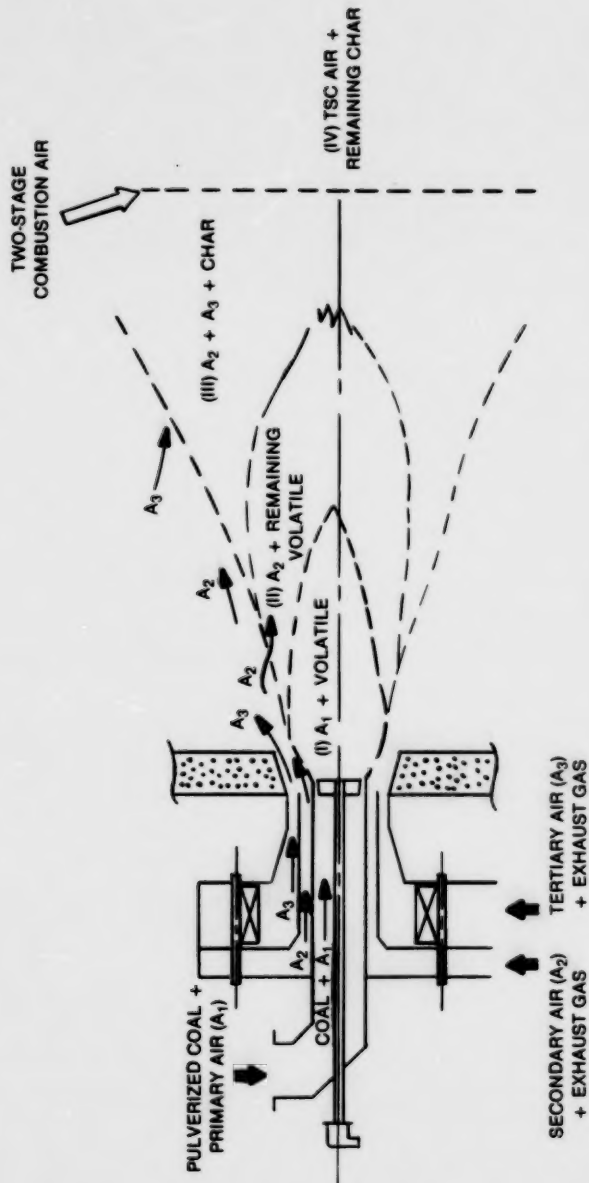


Figure 2-27 Model of Low- $\text{NO}_x$  Pulverized Coal Combustion.

Upon injection of the staged air (IV), the remaining char, CO and other reducing gases are burned. However, no significant amounts of fuel NO<sub>x</sub> or thermal NO<sub>x</sub> are formed during the complete combustion because: 1) virtually all of the nitrogen compounds in the coal already have been decomposed, and 2) the combustion temperature is not very high.

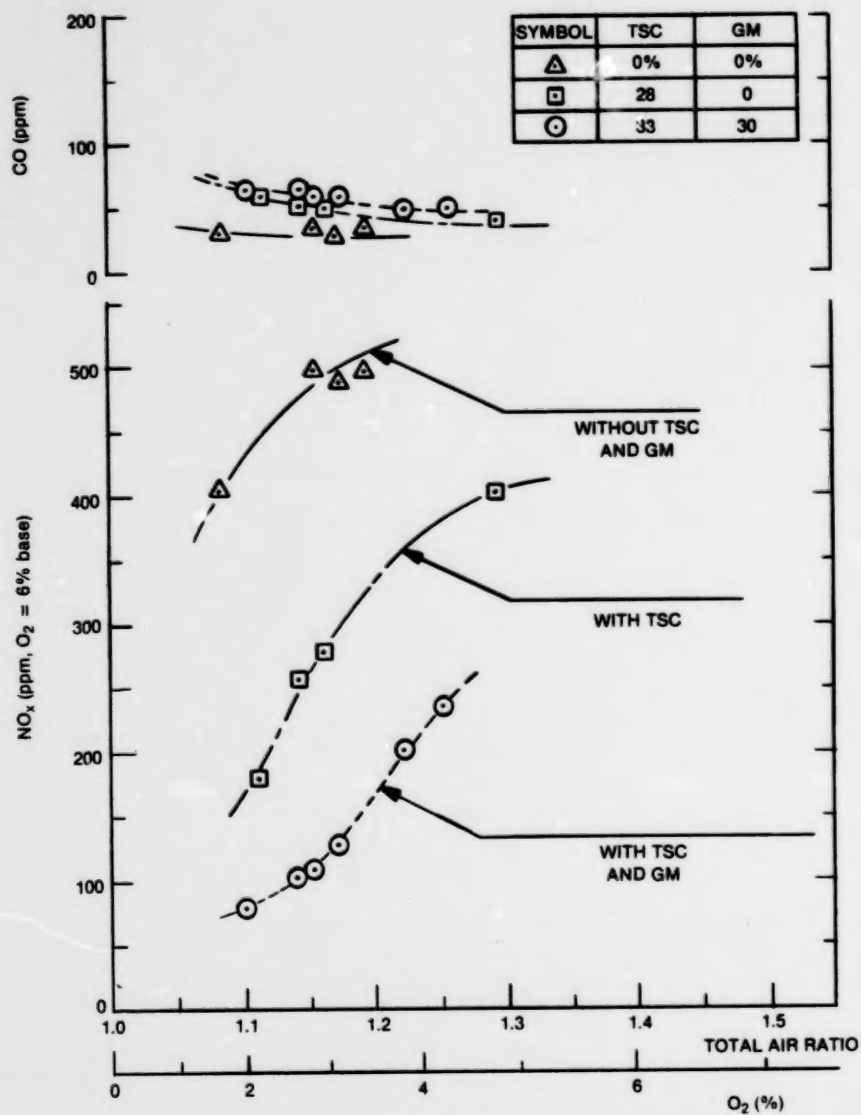
Figure 2-28 shows the test results using the original burner with Japanese coal at the 3t/hr test furnace. The figure clearly illustrates the efficient NO<sub>x</sub> reduction of the burner when used in combination with staged combustion. Flue gas recirculation (gas mixing) further reduced NO<sub>x</sub> concentrations.

Figure 2-29 compares the performance of the original burner with that of the improved VD burner. In the VD burner, the effect of the combined use of staged combustion and gas mixing is greater; a very low NO<sub>x</sub> concentration, below 100 ppm, was achieved. Although the CO concentration in the flue gas increased appreciably, it remained in an acceptable range.

## 2.6 EPDC'S NO<sub>x</sub> ABATEMENT BY COMBUSTION MODIFICATION (10)

### 2.6.1 Introduction

Electric Power Development Co. (EPDC) is a joint venture of the Japanese Government and nine major power companies. One of its objectives is the consumption of domestic coal. EPDC has three power stations which use domestic coal and recently constructed a new station (Matsushima) to use imported coals. The stations and applicable NO<sub>x</sub> regulations are shown in Table 2-8.



TSC: TWO STAGE COMBUSTION GM: GAS MIXING

Figure 2-28 NO<sub>x</sub> Emission Characteristics of Original KHI Burner.

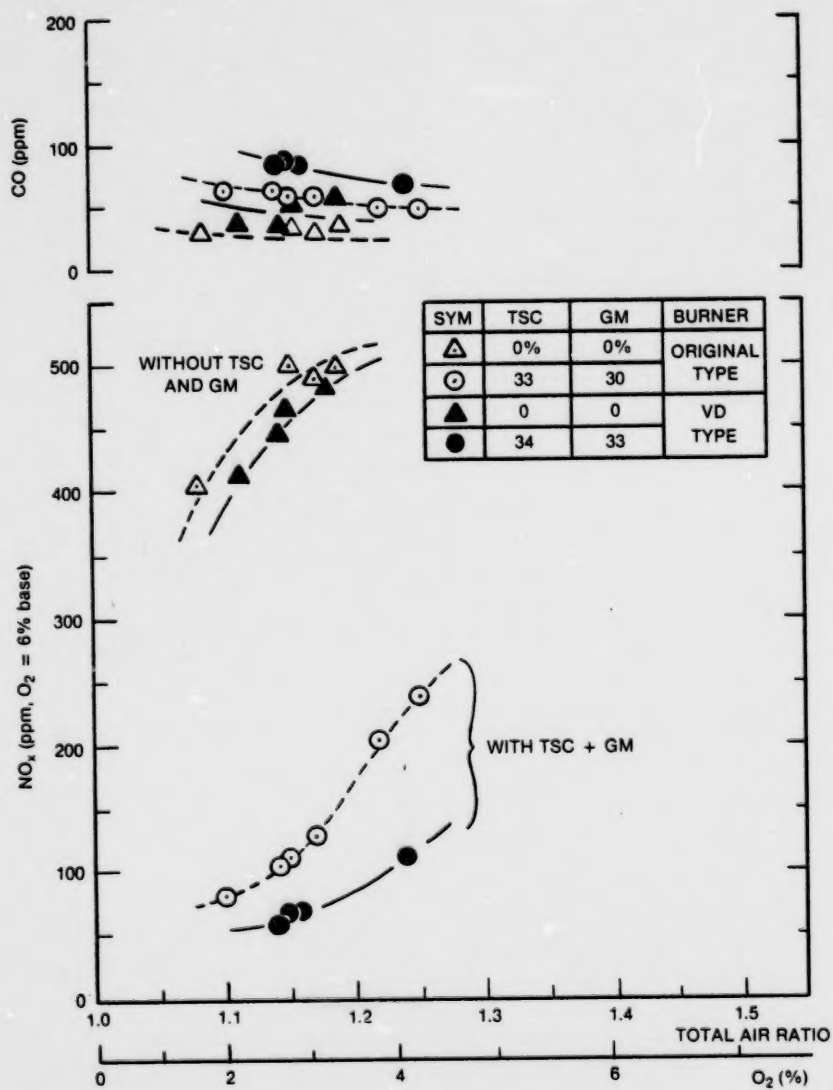


Figure 2-29 Comparison of NO<sub>x</sub> Emissions in VD and Original Burners.

70A2614

TABLE 2-8. EPDC'S POWER STATIONS AND NO<sub>x</sub> REGULATIONS

| Power Station                   | Isogo            |      | Takasago  |      | Takehara         |                  | Matsushima |      |
|---------------------------------|------------------|------|-----------|------|------------------|------------------|------------|------|
| Boiler No.                      | No.1             | No.2 | No.1      | No.2 | No.1             | No.3             | No.1       | No.2 |
| Capacity, MW                    | 265              | 265  | 250       | 250  | 250              | 700              | 500        | 500  |
| Year completed                  | 1967             | 1969 | 1968      | 1969 | 1967             | 1983             | 1980       | 1981 |
| Type of coal                    | Domestic         |      | Domestic  |      | Domestic         | Imported         | Imported   |      |
| NO <sub>x</sub> regulation, ppm |                  |      |           |      |                  |                  |            |      |
| Emission standard               | 400              |      | 400       |      | 400 <sup>b</sup> | 400 <sup>b</sup> | 400        |      |
| Local agreement                 | 159 <sup>a</sup> |      | 300       |      | 112 <sup>b</sup> | 60 <sup>b</sup>  | 300        |      |
| Actual                          | 150-180          |      | Below 300 |      |                  |                  | 240-280    |      |

<sup>a</sup>Under negotiation.

<sup>b</sup>After the completion of the No. 3 boiler in 1982. SCR is to be applied.

#### 2.6.2 Tests of NO<sub>x</sub> Abatement by Combustion Modification

EPDC has conducted extensive tests of combustion modification for NO<sub>x</sub> abatement jointly with major boiler manufacturers including Mitsubishi Heavy Industries (MHI), Babcock Hitachi, Ltd (BHK), Ishikawajima-Harima Heavy Industries (IHI) and Kawasaki Heavy Industries (KHI). Some of the test results are shown in Figure 2-30. Those tests indicate that by using a combination of low-NO<sub>x</sub> burners with staged combustion and flue gas recirculation, NO<sub>x</sub> can be reduced by 60-70%---to 100-150 ppm with low-nitrogen coal and to 150-200 ppm with a nitrogen-rich coal. A test conducted jointly with a company C indicated that flue gas recirculation was not effective for NO<sub>x</sub> abatement with coal, and that unburned carbon increased with the application of staged combustion.

The relationship between polycyclic organic matter (POM) concentrations and NO<sub>x</sub> concentrations is shown in Figure 2-31. POM generally increased with the decrease in NO<sub>x</sub> caused by combustion modification. Table 2-9 shows the POM compounds and their relationship to combustion modification.



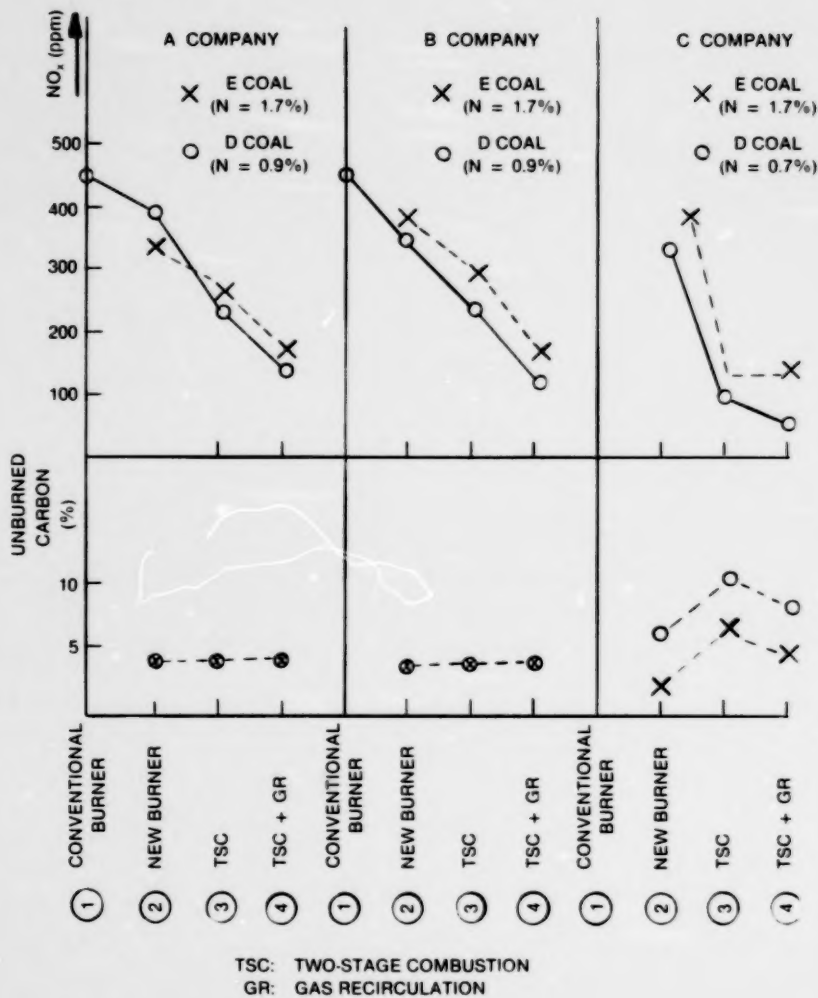
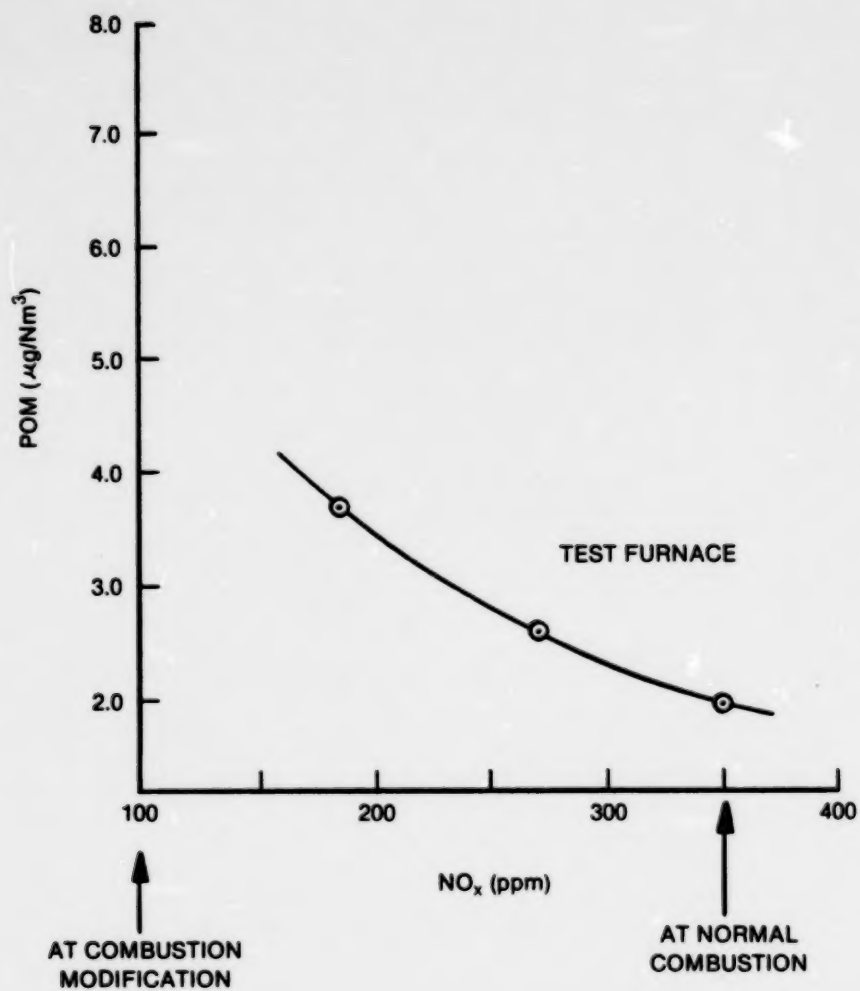


**Figure 2-30 Examples of Combustion Modification Tests Conducted by EPDC and Boiler Manufacturers.**



( $\text{NO}_x$  concentration in test furnace is the average value of maximum and minimum values.)

**Figure 2-31**  $\text{NO}_x$  Concentration vs. P.O.M. Emission.

70A2616

TABLE 2-9. MEASUREMENT RESULTS OF POM AT FURNACES (Unit  $\mu\text{g}/\text{Nm}^3$ )

| POM Component                                                 | Combustion Condition | Normal Combustion | 2 Stage Combustion | 2 Stage + FG Mix + Primary Gas | PGM           | Partial Load  |
|---------------------------------------------------------------|----------------------|-------------------|--------------------|--------------------------------|---------------|---------------|
| Naphthalene                                                   |                      | 0.22              | 0.18               | 0.22                           | 0.24          | 0.24          |
| Fluoranthene                                                  |                      | —                 | 0.40               | 0.88                           | 0.78          | 0.84          |
| Pyrene                                                        |                      | 0.65              | 0.64               | 0.87                           | 0.87          | 0.84          |
| Benzo (a) pyrene                                              |                      | 0.48              | 0.59               | 0.66                           | 0.58          | 0.62          |
| Total POM<br>(Percentage when<br>Normal combustion<br>is 100) |                      | 1.99<br>(100)     | 2.62<br>(132)      | 2.46<br>(124)                  | 3.15<br>(158) | 3.49<br>(175) |

Although the POM concentration increased with combustion modification, it reached a much lower level than the values reported in the U.S. POM was measured using the EPA No. 5 sampling method, modified by Battelle, and a liquid chromatography analyzer. It is not clear whether the difference in values is due to the analytical method (GC-MS was used in the U.S.) or to differences in the type of coal and the size of boiler used.

#### 2.6.3 Combustion Modification at Isogo Power Station

The Isogo Power Station, located in Yokohama City (population 4 million) was asked by the city to reduce  $\text{NO}_x$  emissions as much as possible. The station had no space to install SCR units because FGD plants had already been retrofitted in the narrow spaces beside the boilers. Therefore, extensive efforts have been made to reduce  $\text{NO}_x$  by combustion modification.

The specifications of the Isogo boilers are given in Table 2-10. The boilers burn domestic low-sulfur coal which is relatively low in nitrogen and volatile matter and is suitable for  $\text{NO}_x$  abatement (Table 2-11).

**TABLE 2-10. SPECIFICATIONS FOR ISOGO 265 MW PULVERIZED COAL-FIRED BOILER**

---

|                               |                                                                                             |
|-------------------------------|---------------------------------------------------------------------------------------------|
| Type:                         | IHI-FW single drum, radiant type,<br>natural circulation, reheat boiler<br>(indoor service) |
| Evaporation (at M.C.R.):      | 840,000 kg/h                                                                                |
| Steam pressure (at M.C.R.)    |                                                                                             |
| Superheater outlet:           | 176 kg/cm <sup>2</sup> g                                                                    |
| Reheater outlet:              | 34 kg/cm <sup>2</sup> g                                                                     |
| Steam temperature (at M.C.R.) |                                                                                             |
| Superheater outlet            | 571°C                                                                                       |
| Reheater outlet               | 571°C                                                                                       |
| Fuel:                         | Bituminous coal (equipped with 50% MCR<br>heavy oil firing system)                          |
| Number of burners:            | 24 set (4 rows and 3 stages on boiler<br>front and rear walls)                              |
| Draft System:                 | Balance draft system                                                                        |

---

The boilers were completed in 1967 and 1969, and were modified in 1973 with an over-fire air port system for NO<sub>x</sub> abatement. As a second step to meet the increasingly stringent NO<sub>x</sub> regulation, an IHI-FW DF-CN burner (Section 2.2) and a boundary air system (Figure 2-32) were applied to the No. 1 boiler in 1976 and to the No. 2 boiler in 1977. The boundary air prevents the melting of the ash. As a third step, burners out of service (BOOS) and steam injection from oil guns were tested on the No. 2 boiler in 1978. Eight additional over-fire air ports also were installed near the side walls and a division wall, based on tests conducted by IHI. In addition, steam injection was carried out through oil burner guns for the No. 2 boiler. These modifications were made in the spring of 1979 to reduce NO<sub>x</sub> below 180 ppm (at 6% O<sub>2</sub>) under routine operating conditions. The same modifications were made on the No. 1 boiler in 1980. The results of these modifications are summarized in Table 2-12.

TABLE 2-11. TYPICAL ANALYSIS OF COAL USED AT ISOGO STATION

|                      |               |
|----------------------|---------------|
| Higher heating value | 6,200 kcal/kg |
| Ash                  | 16.5%         |
| Volatile matter      | 39.6%         |
| Fixed carbon         | 39.4%         |
| Sulfur               | 0.4%          |
| Hydrogen             | 5.5%          |
| Nitrogen             | 1.0%          |

TABLE 2-12. MODIFICATIONS MADE FOR INCREASED NO<sub>x</sub> CONTROL AT THE ISOGO POWER UNIT

| Month, Year     | NO <sub>x</sub> Emission Level by Regulation, etc. (ppm) | Achieved NO <sub>x</sub> Level (ppm) | Modifications                                 |
|-----------------|----------------------------------------------------------|--------------------------------------|-----------------------------------------------|
| Before May 1973 | 600                                                      | 570                                  | None                                          |
| June, 1973      | 600                                                      | 380 ~ 510                            | Two-Stage combustion                          |
| April, 1977     | 480                                                      | 240 ~ 250                            | Low-NO <sub>x</sub> burner<br>Curtain Air     |
| April, 1979     | 400                                                      | 170 ~ 190                            | More rigorous<br>Two-Stage<br>combustion, etc |
| April, 1980     | 159 <sup>a</sup>                                         | 170 ~ 190                            |                                               |

<sup>a</sup>Yokohama City's Requirement

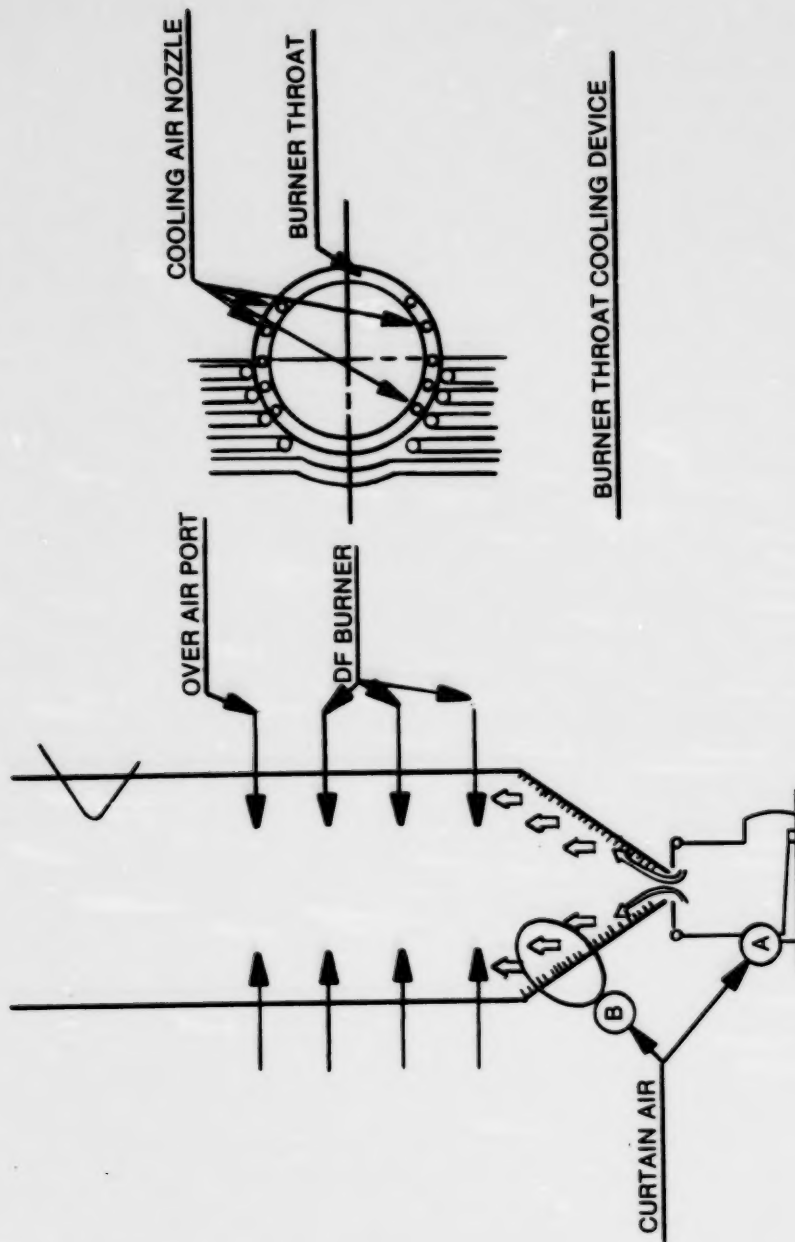


Figure 2-32 IHI's Boundary Air System and Burner Throat Cooling Device.



Figure 2-33 shows the relationship between the overfire air port open ratio and NO<sub>x</sub> emissions. With the 50% opening, NO<sub>x</sub> is reduced to 150-180 ppm. By increasing the size of the opening, NO<sub>x</sub> can be further lowered, but the super-heater tube metal temperature becomes excessively high. To prevent overheating of the superheater, methods of modifying the superheater layout, were tested; unfortunately test results were not very successful. Figure 2-34 shows NO<sub>x</sub> and O<sub>2</sub> concentrations during the actual operation of the boiler. NO<sub>x</sub> is maintained around 170 ppm at full load and 140 ppm at the reduced load. Although the NO<sub>x</sub> concentration increased during the load change, it seldom exceeded 200 ppm.

#### 2.6.4 Matsushima Power Station

Two new 500 MW coal-fired boilers were completed at the Matsushima Station in late 1980, and went into commercial operation in 1981. The boilers were constructed by MHI using tangential-firing and SGR burners (Section 2.4.1). The specifications of the boilers are shown in Table 2-13. NO<sub>x</sub> concentrations of 200-290 ppm were attained during test operation using imported coal containing 1.7% nitrogen. In commercial operation, NO<sub>x</sub> has been kept below 290 ppm to meet the local agreement of 300 ppm.

TABLE 2-13. SPECIFICATIONS OF BOILERS AT MATSUSHIMA POWER STATION

|                                   |                                                   |
|-----------------------------------|---------------------------------------------------|
| Output, MW                        | 500 x 2 unit                                      |
| Fuel                              | Coal (imported)                                   |
| Boiler Manufacturer               | MHI                                               |
| Type of Boiler                    | Supercritical pressure reheat type<br>U.P. boiler |
| NO <sub>x</sub> (guaranteed), ppm | 285 (O <sub>2</sub> = 6%) (N = 1.7%)              |
| NO <sub>x</sub> (target)          | same as guaranteed                                |
| Burner type                       | SGR burner (illustrated in Section 2.4.1)         |

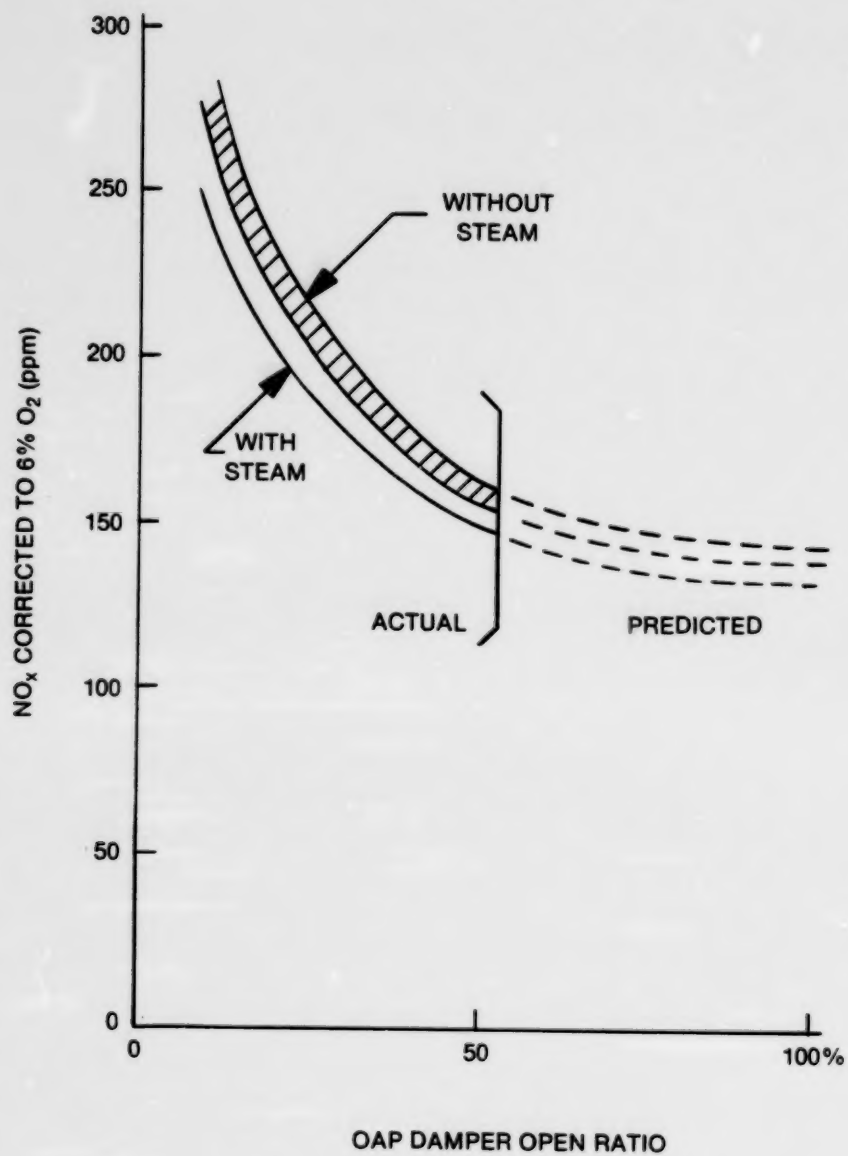


Figure 2-33 Damper Open Ratio and NO<sub>x</sub> Concentration. (Isogo)

DATE FEB. 18, '80

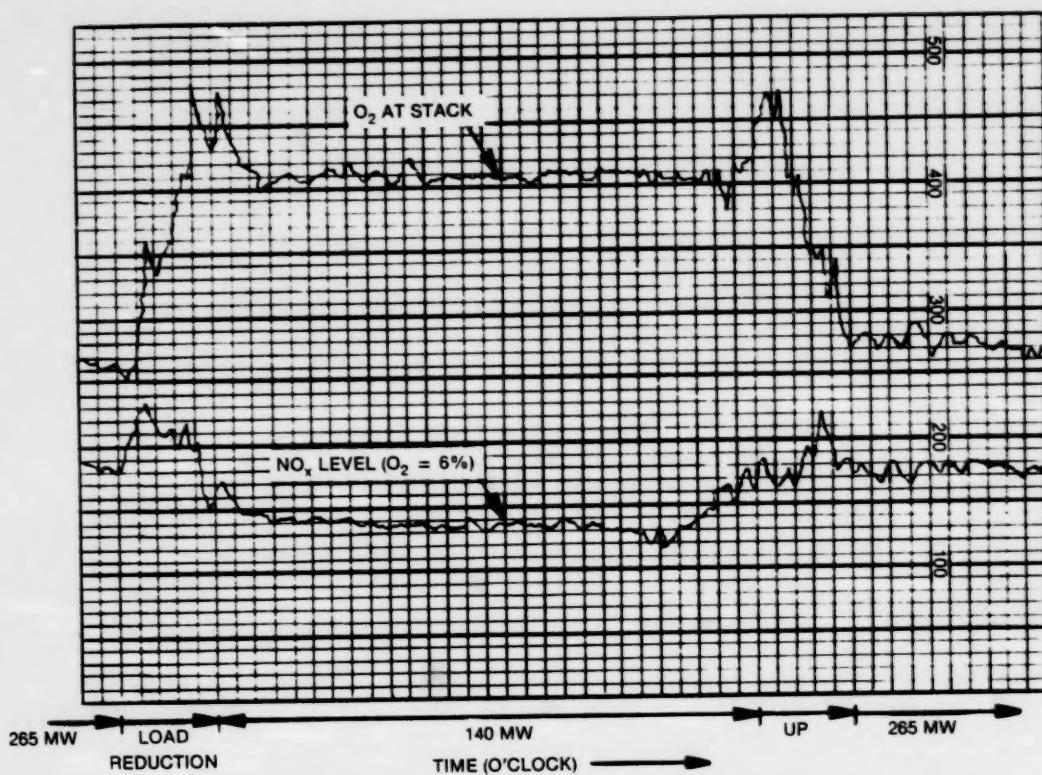


Figure 2-34 NO<sub>x</sub> Concentrations During Boiler Operation. (Isogo)

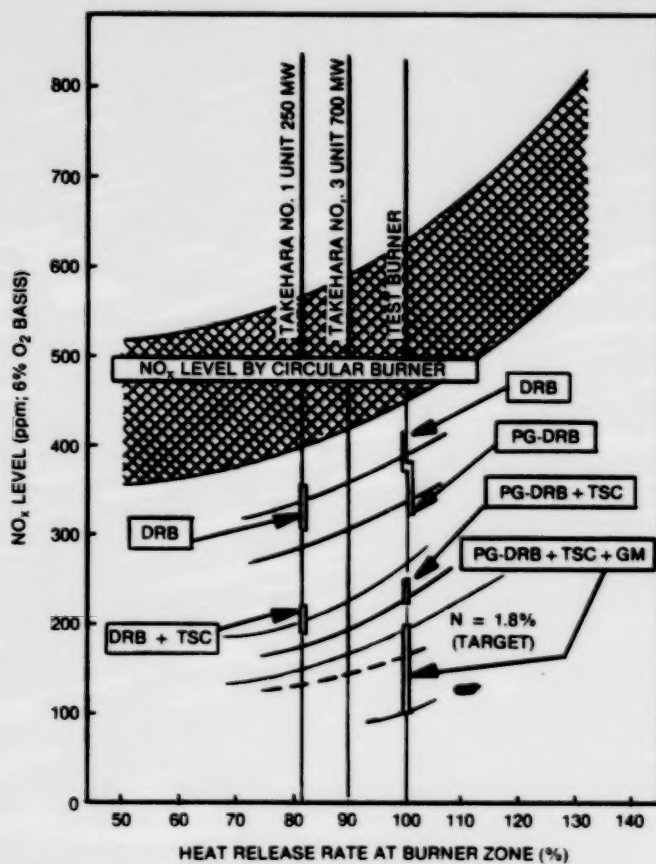
### 2.6.5 Takehara Power Station

The Takehara Station has a 250 MW coal-fired boiler (No. 1) and a 350 MW oil-fired boiler (No. 2). In addition, EPDC has begun construction of the No. 3 Unit, a 700 MW coal-fired boiler. Many NO<sub>x</sub> abatement techniques for the coal-fired boilers are planned, including the application of SCR. Specifications for the No. 3 boiler are shown in Table 2-14. The boiler is being constructed by Babcock-Hitachi (BHK) and is scheduled for completion late in 1982; it will begin commercial operation in March 1983.

TABLE 2-14. SPECIFICATIONS OF NO. 3 BOILER OF TAKEHARA STATION

|                                             |                                                  |
|---------------------------------------------|--------------------------------------------------|
| Output, MW                                  | 700 x 1 unit                                     |
| Fuel                                        | Coal (imported coal)                             |
| Boiler Manufacturer                         | BHK                                              |
| SCR Manufacturer                            | BHK                                              |
| Type of Boiler                              | B&W Supercritical pressure reheat type UP boiler |
| NO <sub>x</sub> (guaranteed at boiler), ppm | 250 (O <sub>2</sub> = 6%, N = 1.8%)              |
| NO <sub>x</sub> (target at boiler), ppm     | 200 (O <sub>2</sub> = 6%, N = 1.8%)              |
| NO <sub>x</sub> (guaranteed at stack), ppm  | 60 and below (O <sub>2</sub> = 6%, N = 1.8%)     |
| Burner type                                 | PG dual burner                                   |

The Takehara Power Station uses PG dual-air register burners (Section 2.3). Figure 2-35 shows the relationship between the heat release rate at the burner zone and NO<sub>x</sub> concentrations with three types of burners—conventional circular-air register, dual-air register, and PG dual-air register—with or without two-stage combustion and gas mixing. The No. 1 boiler uses a dual-air register burner and produces about 200 ppm NO<sub>x</sub> using two-stage combustion, and about 300-360 ppm NO<sub>x</sub> without two-stage combustion. A test furnace with a higher heat release rate produced about 400 ppm NO<sub>x</sub> with the dual-air register burner and around 350 ppm NO<sub>x</sub> with the PG-type burner when staged combustion was not applied; it produced 100-200 ppm NO<sub>x</sub> with the



CB: CIRCULAR AIR  
REGISTER BURNER  
DRB: DUAL AIR  
REGISTER BURNER  
PG-DRB: PG TYPE-DRB  
TSC: TWO-STAGE COMBUSTION  
GM: GAS MIXING TO  
SECONDARY AIR

Figure 2-35 Heat Release Rate at Boiler Zone. (%)

PG-type burner with staged combustion and gas mixing. Since the heat release rate of the No. 3 boiler falls between that of the No. 1 boiler and the test furnace, a  $\text{NO}_x$  concentration about 150 ppm or below is expected.

## 2.7 LOW- $\text{NO}_x$ BURNERS FOR GAS AND OIL FIRING

### 2.7.1 Introduction

Various types of low- $\text{NO}_x$  burners for gas- and oil-fired boilers have been developed and used in Japan. These burners may be classified into the following categories according to the principles of  $\text{NO}_x$  abatement employed.

- (1) High-mixing
- (2) Divided-flame
- (3) Self-recirculating
- (4) Staged-combustion
- (5) Off-stoichiometric-combustion
- (6) Water-injection
- (7) Combination

This section describes the major low- $\text{NO}_x$  burners available for commercial gas- and oil-firing applications.

### 2.7.2 High-Mixing Burner

A high-mixing burner developed by Nippon Furnace Kogyo Kaisha, Ltd. is shown in Figure 2-36. It is called a NFK-TRW burner, because it was developed by Nippon Furnace jointly with TRW Inc. of the U.S., under a licensing agreement with Civiltech Corp. of the U.S.

$\text{NO}_x$  concentrations for the burner using oil under various operating conditions are shown in Figure 2-37. This burner reduces the formation of thermal  $\text{NO}_x$  by shortening the residence time of the combustion gas in high-temperature zones.



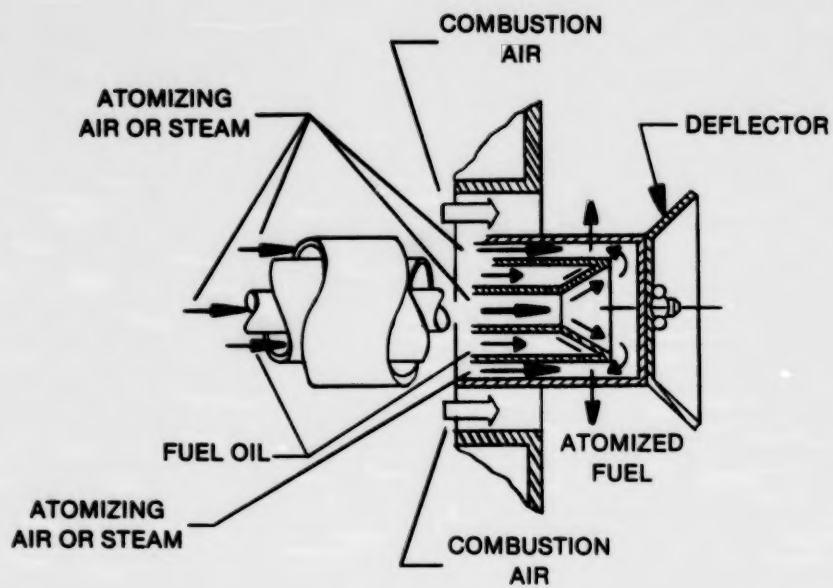
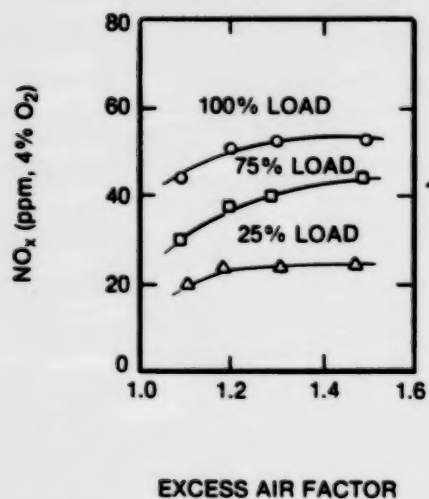


**Figure 2-36 NFK-TRW Burner.**



(Fuel: Grade A fuel oil; air temperature: 25°C;  
maximum fuel flow rate: 380 l/hr)

**Figure 2-37** Effect of NFK-TRW Burner on NO<sub>x</sub> Concentrations.

70A2551

### 2.7.3 Divided-flame Burner

A divided-flame burner developed by IHI is shown in Figure 2-38. In this burner the flame is divided into several small flames by means of grooved nozzle tips. This reduces the flame temperature and residence time in high-temperature zones, thus reducing thermal  $\text{NO}_x$  (13).

### 2.7.4 Self-recirculating Burner

In the self-circulating burner, a portion of the hot combustion gas is recirculated to the initial stage of combustion by the jet force of the fuel and/or air injection. Thus vaporization and burning of the fuel oil in a low  $\text{O}_2$  concentration are achieved. Various burners of this type have been produced by many manufacturers.

Figure 2-39 shows the configuration of the burner developed by Daido Tokushuko (Special Steel) Co. The  $\text{NO}_x$  concentration with this burner is shown in Figure 2-40. The burner was originally developed for metal-heating furnaces firing oil or gas. A similar burner called the SPP has been developed by the Volcano Company.

The burner shown in Figure 2-41 produces a circulating flow of combustion gas in the precombustion chamber by means of orienting the air flow with intense swirls to the axis of the atomizer. It is called a voltmetric burner and was commercialized by Nippon S. T. Johnson Shokai Co., Ltd.

Similar burners, designed for kerosene firing, are shown in Figures 2-42 and 2-43. The NPL burner was developed by Chugairo Kogyo, Ltd., and the YLAP burner by Yokoi Kikai Kosakujo, Ltd. The  $\text{NO}_x$  levels with the NPL burner are shown in Figure 2-44. These burners use low air-pressure atomizers with various burner tile configurations.

Figure 2-45 shows the ONR burner with a rotary atomizer, developed by Sanrey Reinetsu Co., Ltd. Combustion gas is recirculated by the secondary air jet at a high velocity. The burner's performance is shown in Figure 2-46.

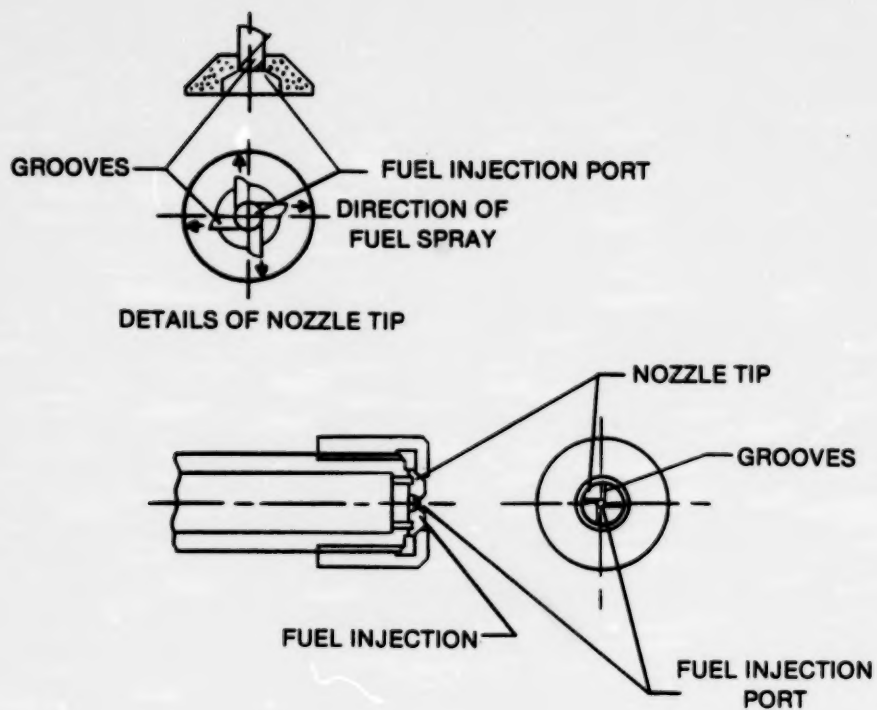


**Figure 2-38 IHI Divided Flame Burner.**

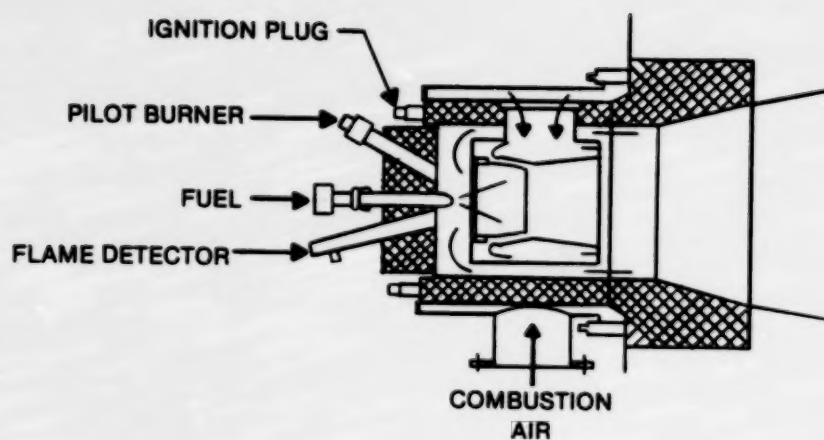
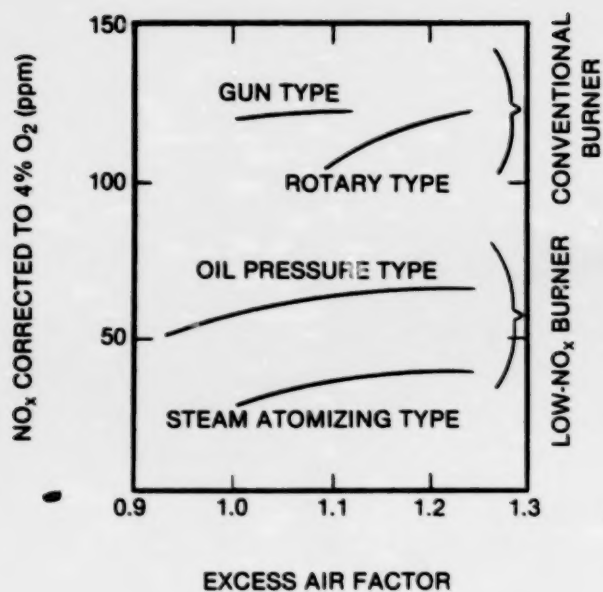


**Figure 2-39** Daido Tokushuko Self-recirculation Burner.



(Fuel: Grade A oil; fuel flow rate: 100 l/hr)

**Figure 2-40 Effect of Self-recirculation Burner on NO<sub>x</sub> Reduction.**



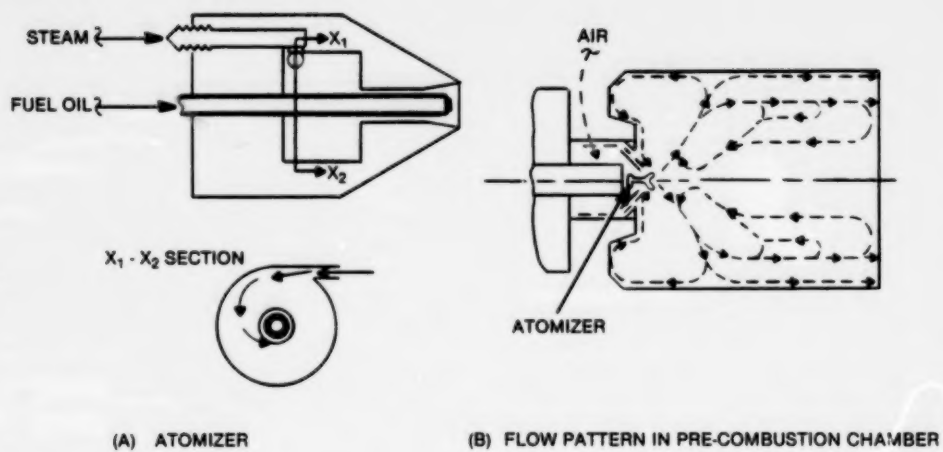


Figure 2-41 Schematic Diagram of the Voltmetric Burner (Nippon S.T. Johnson).

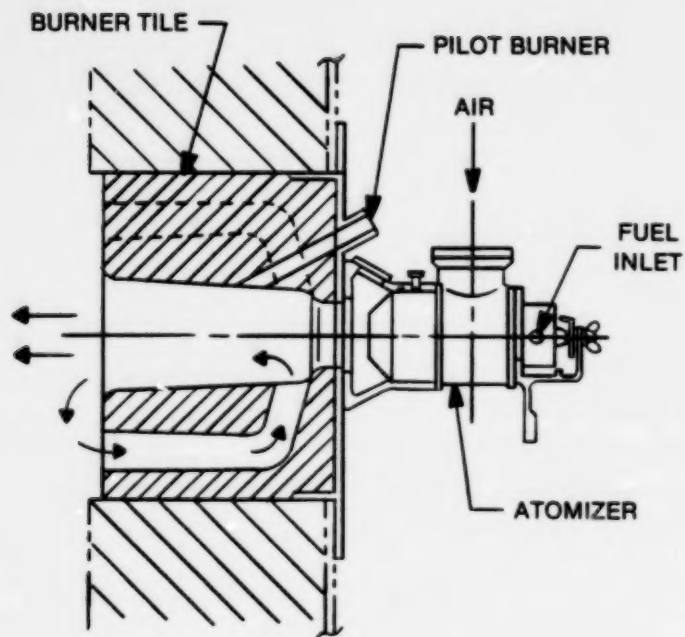


**Figure 2-42 NPL Burner (Chugairo Kogyo).**

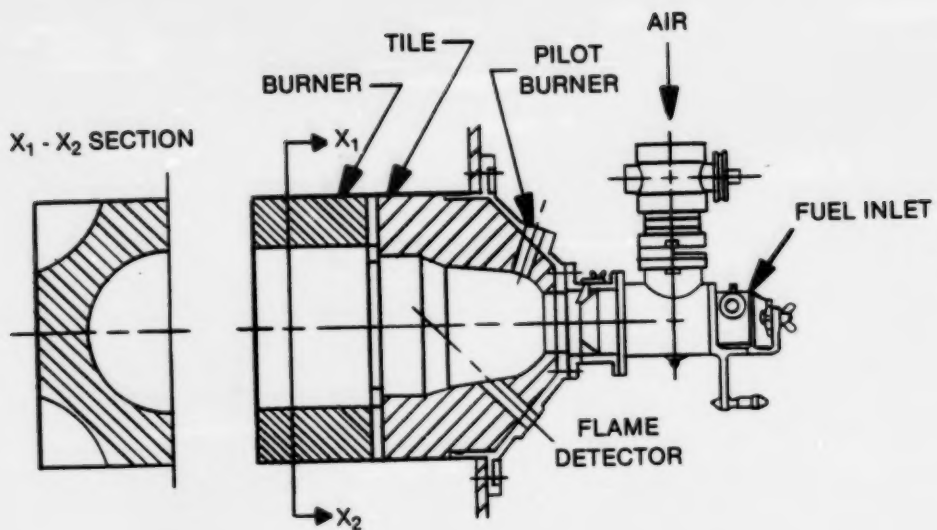
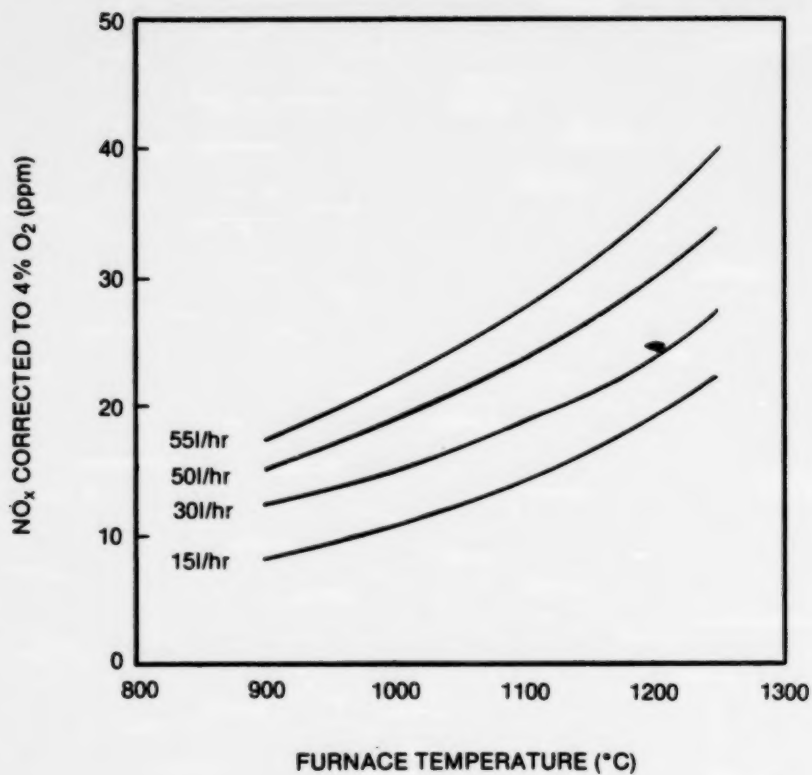


Figure 2-43 YLAP Burner (Yokoi Kikai Kosakujo).



(Fuel: kerosene; oxygen concentration in the outlet of test furnace: 3%; fuel flow rate: 15 l/hr - 55 l/hr)

**Figure 2-44 Effect of NPL Burner on NO<sub>x</sub> Emissions.**

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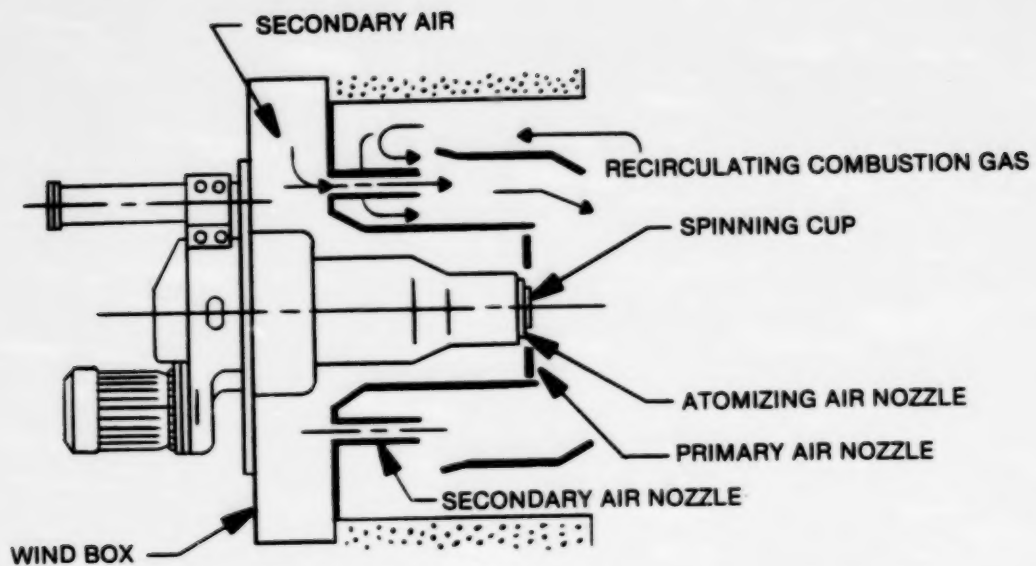
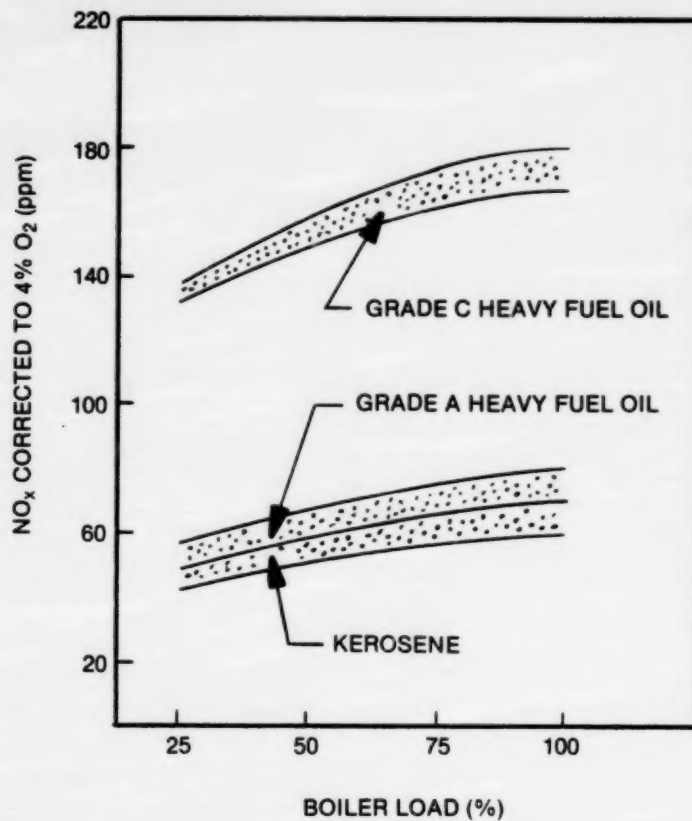


Figure 2-45 ONR Burner (Sanrey Reinetsu).



(Fuel flow rate: 700-1000 kg/hr; excess air factor: 1.10-1.15;  
combustion air temperature: 20°C)

**Figure 2-46 NO<sub>x</sub> Emission Level of ONR Burner.**



Figure 2-47 shows the RSNT burner designed by Rozai Kogyo Co. for oil and gas firing. An intense swirling flow of secondary air causes the recirculation of the combustion gas in the narrow space confined by the burner tile.  $\text{NO}_x$  emission levels by fuel type are shown in Figure 2-48.

Figure 2-49 shows the XB burner developed by Osaka Gas Co. jointly with Sanrei Reinetsu Co. for gas-firing applications. Several fuel injection nozzles are arranged circularly to shorten the flame. A low  $\text{NO}_x$  level, 20-40 ppm, is achieved, as shown in Figure 2-50.

The High Speed burner, developed by Tokyo Gas Co., is shown in Figure 2-51. Flue gas is recirculated by the momentum of the fuel flow and a large amount of combustion gas is entrained by the high-velocity gas flow.

#### 2.7.5 Staged-Combustion Burner

The staged-combustion burner may be classified according to the composition of the first-stage flame into two types: fuel-rich and air-rich. The fuel-rich burner is similar to the standard staged combustion burner. Both fuel  $\text{NO}_x$  and thermal  $\text{NO}_x$  are lowered by fuel-rich combustion followed by complete combustion at relatively low temperatures. With the air-rich burner, the first stage has an excessive  $\text{O}_2$  concentration and additional fuel is injected during the second stage.

##### Fuel-Rich Type

Figure 2-52 shows the APOC burner developed by Tokyo Gas Company for gas-firing applications. In the pre-combustion chamber, an excess air factor of 0.5 to 0.7 is used.  $\text{NO}_x$  concentrations in the flue gas after complete combustion are about 35 ppm (corrected to 5%  $\text{O}_2$ ).

Figures 2-53 and 2-54 show the FH burner developed by Chugairo Kogyo, Ltd., and its performance. A high  $\text{NO}_x$  reduction efficiency, 75-80%, can be achieved with this burner when used with certain types of furnaces.

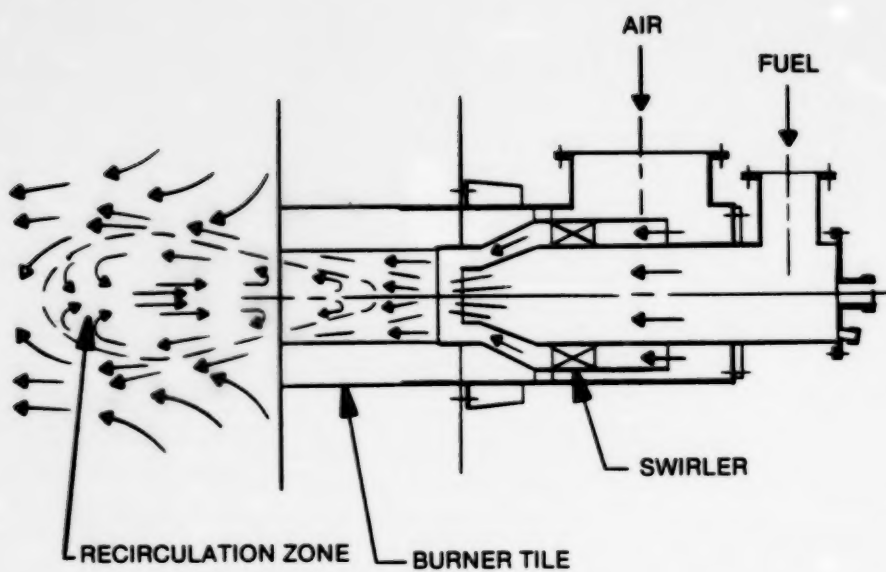


Figure 2-47 RSNT Burner (Rozai Kogyo).

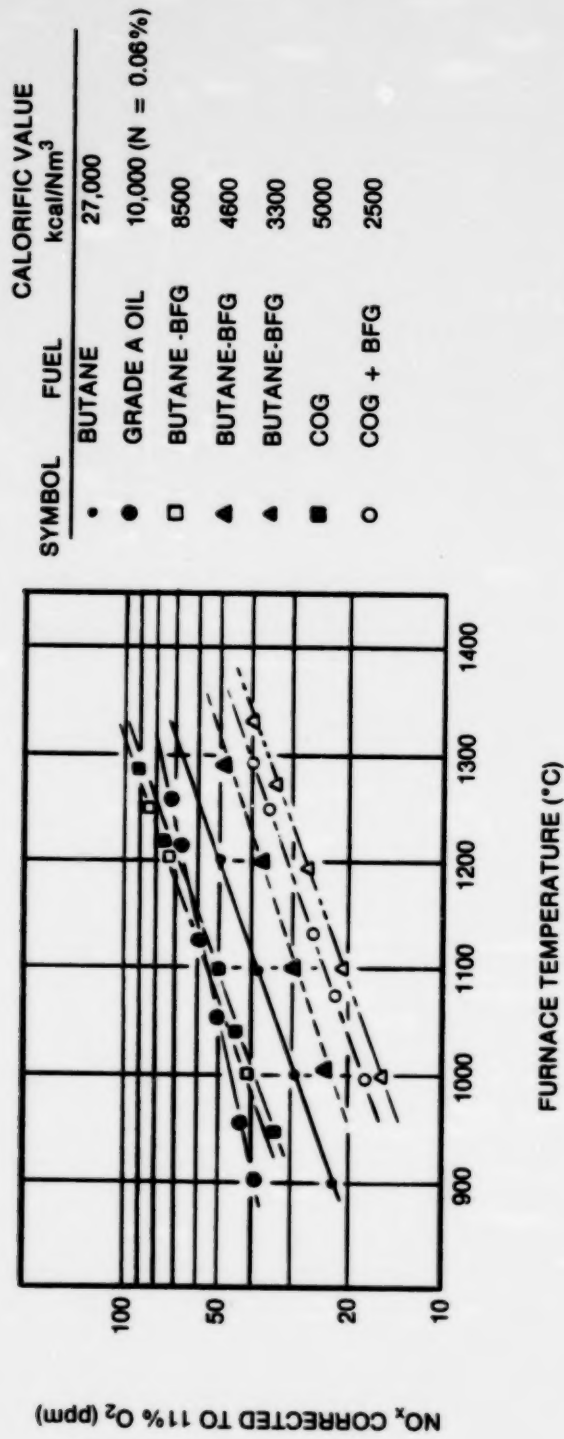


Figure 2-48 NO<sub>x</sub> Emission Levels of the RSNT Burner. (Thermal Input:  $2.4 \times 10^6$  kcal/h; excess air factor: 1.1; combustion air temperature: 250-350°C).

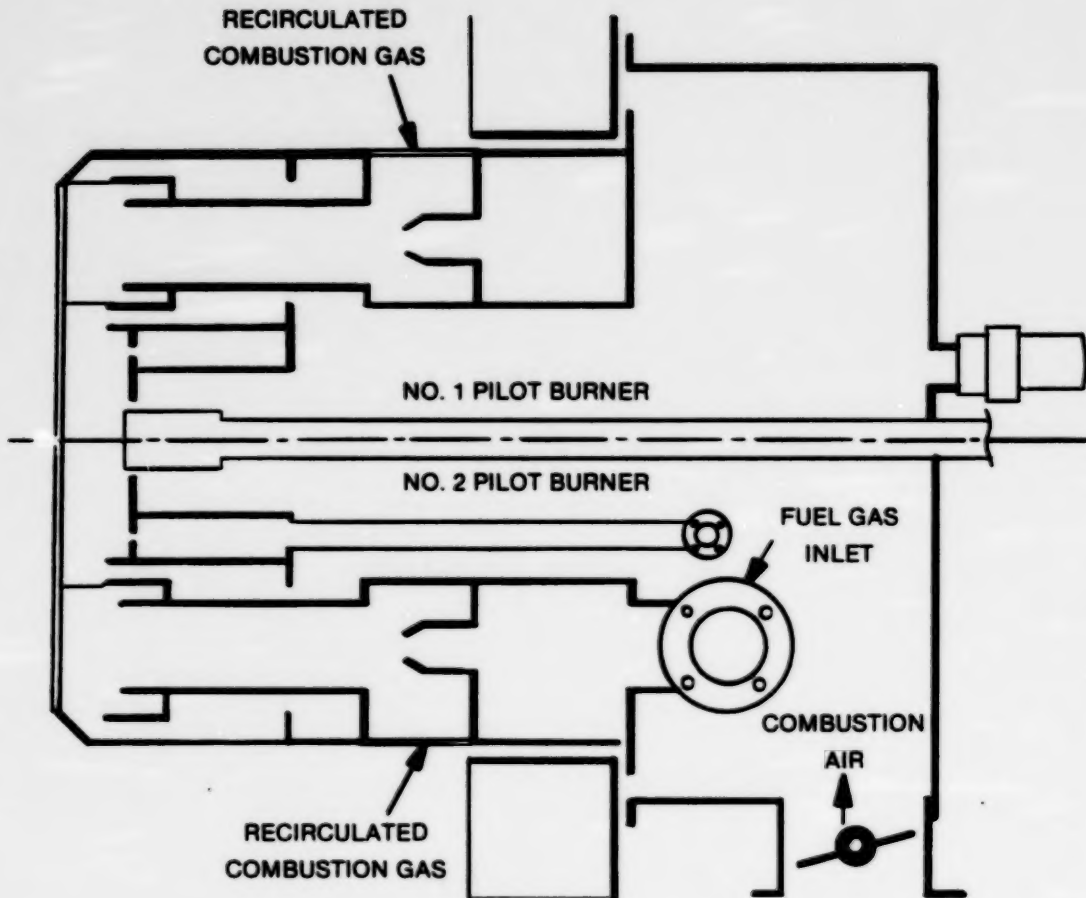


**Figure 2-49** XB Burner (Osaka Gas).

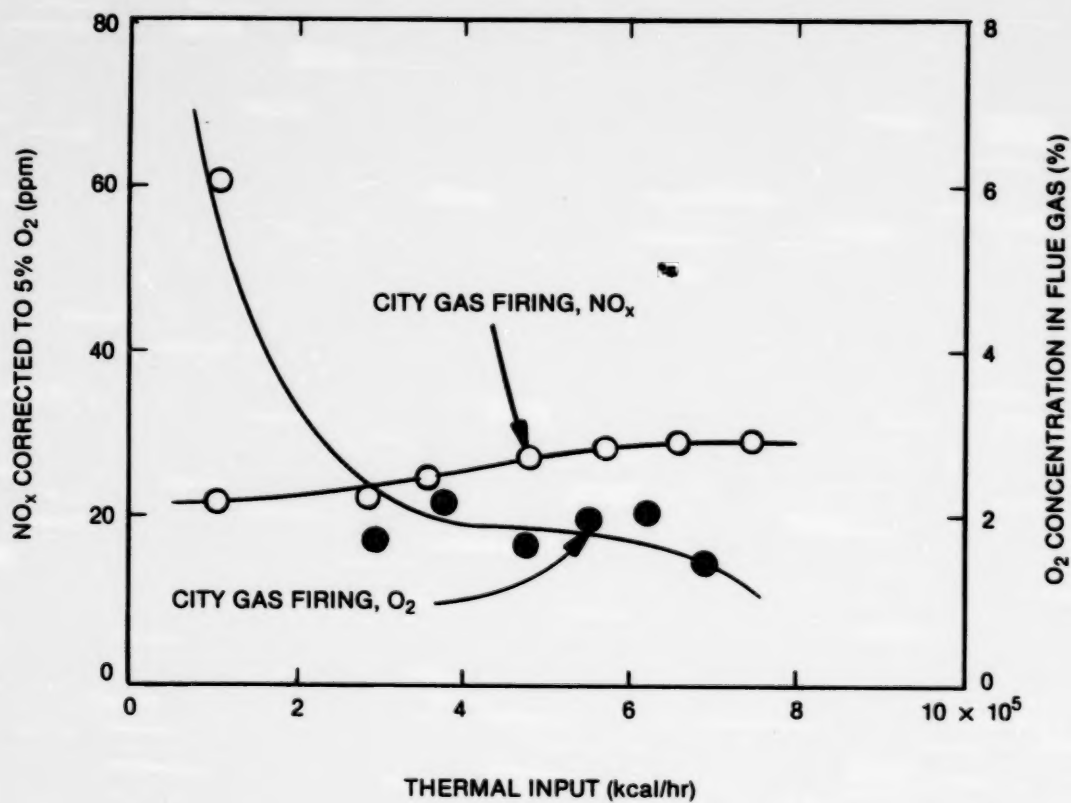


Figure 2-50 Effect of XB Burner on NO<sub>x</sub> Emission Levels.

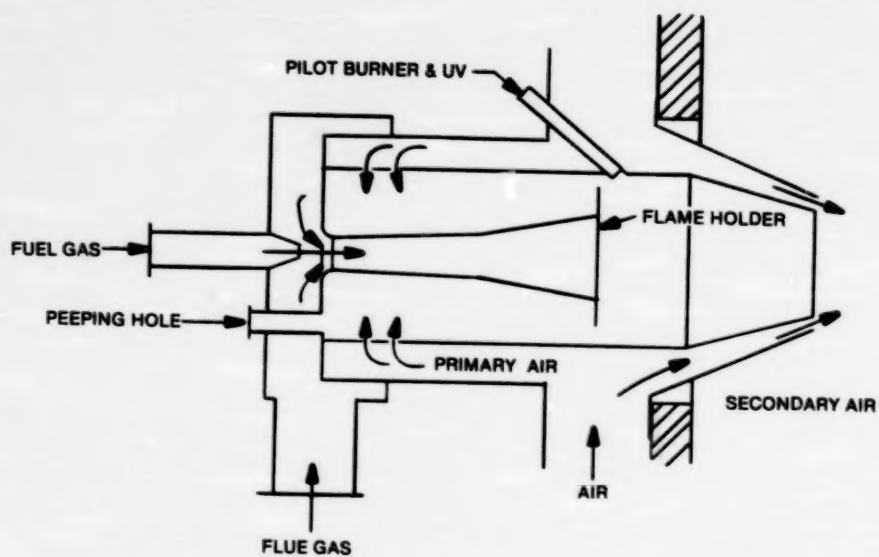


Figure 2-51 High Speed Burner (Tokyo Gas).



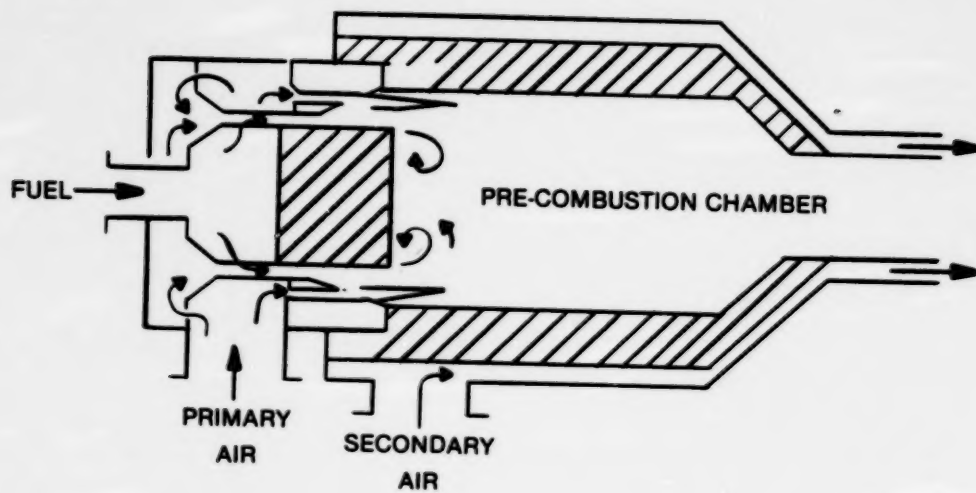


**Figure 2-52** APOC Burner (Tokyo Gas).

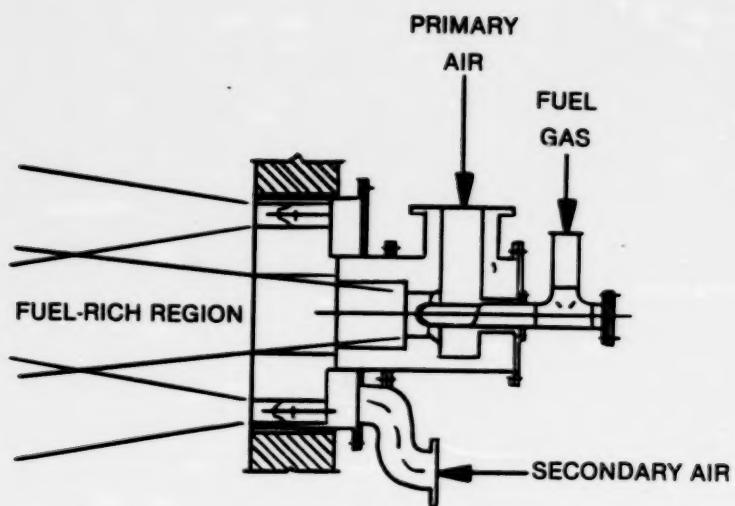


**Figure 2-53**      **Schematic of FH Burner (Chugairo Kogyo).**

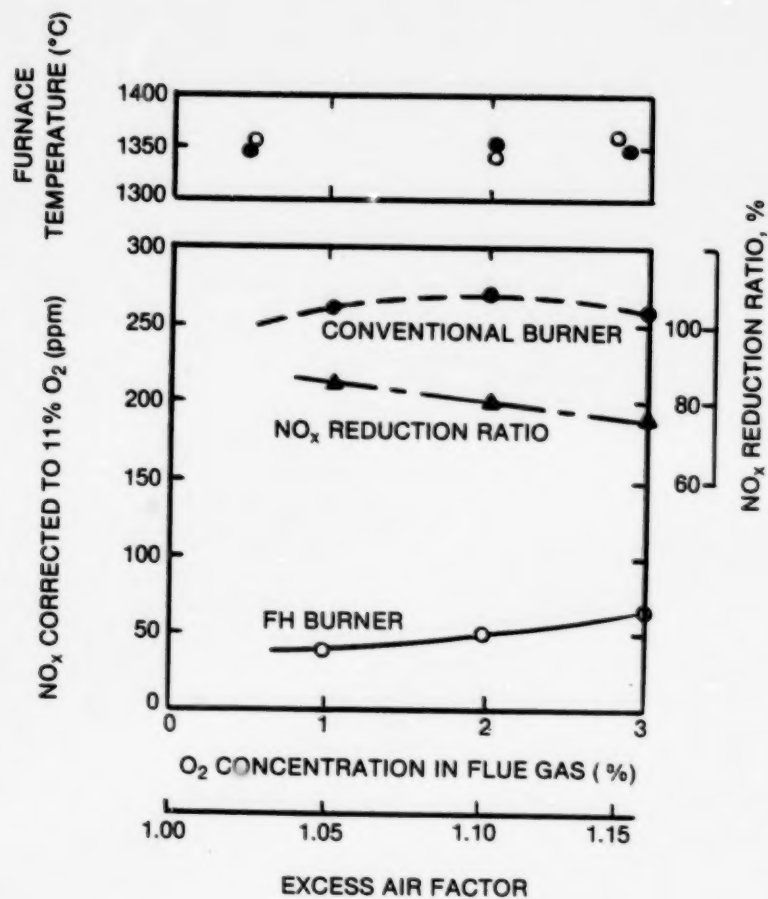


FIGURE 2-54 Effect of the FH Burner on NO<sub>x</sub> Reduction.

Figure 2-55 shows the MR burner developed by MHI for package boilers with a capacity of up to 30 t/hr. In addition to producing the effect of staged combustion, this burner also reduces  $\text{NO}_x$  by cooling the flame with an adjacent water tube. The  $\text{NO}_x$  levels guaranteed by MHI are shown in Table 2-15.

The TS burner developed by Osaka Gas Co. and its performance are shown in Figures 2-56 and 2-57.

TABLE 2-15.  $\text{NO}_x$  EMISSION LEVELS GUARANTEED WITH THE MR BURNER FOR SMALL SCALE BOILERS

| Fuel        | Nitrogen Content in Fuel (%) | $\text{NO}_x$ Emission Level (ppm) |
|-------------|------------------------------|------------------------------------|
| Grade C Oil | 0.20                         | 150 <sup>a</sup>                   |
| Grade B Oil | 0.14                         | 130 <sup>a</sup>                   |
| Grade A Oil | 0.03                         | 65-90 <sup>a</sup>                 |
| Kerosene    | 0.01                         | 60-70 <sup>a</sup>                 |
| Gas         | —                            | 50 <sup>b</sup>                    |

<sup>a</sup>Corrected to 4%  $\text{O}_2$ .

<sup>b</sup>Corrected to 5%  $\text{O}_2$ .

#### Air-Rich Type

Figure 2-58 shows the TGS burner developed by the Tokyo Gas Company. The primary fuel gas is premixed with a large amount of excess air. The rest of the gas is then added to the flame. The burner shows an appreciable  $\text{NO}_x$  reduction as illustrated in Figure 2-59.

Figure 2-60 shows the TZ burner developed by the Daido Sanso Company. In the primary combustion chamber, 40-60% of the fuel is fired with a large amount of excess air—a factor of 1.6 to 2.4—and the secondary fuel injected into the furnace is burned with an  $\text{O}_2$  concentration of 7-14%. The overall excess air ratio is kept between 1.05 and 1.2. The performance of the burner is shown in Figure 2-61.

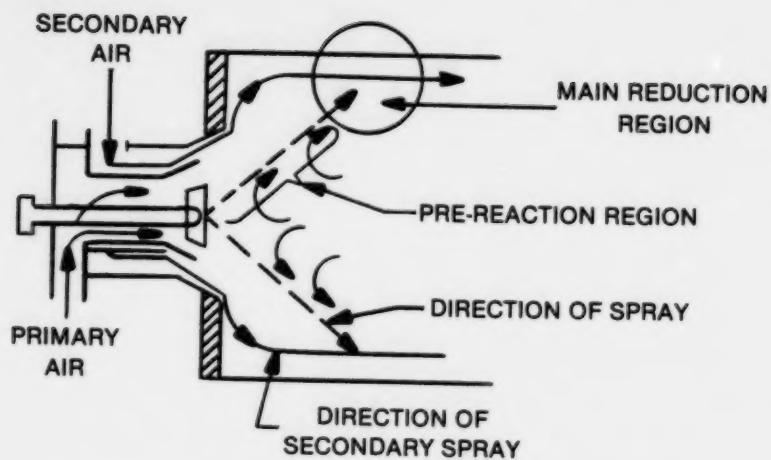


**Figure 2-55 Schematic of MR Burner (Mitsubishi Heavy Industries).**

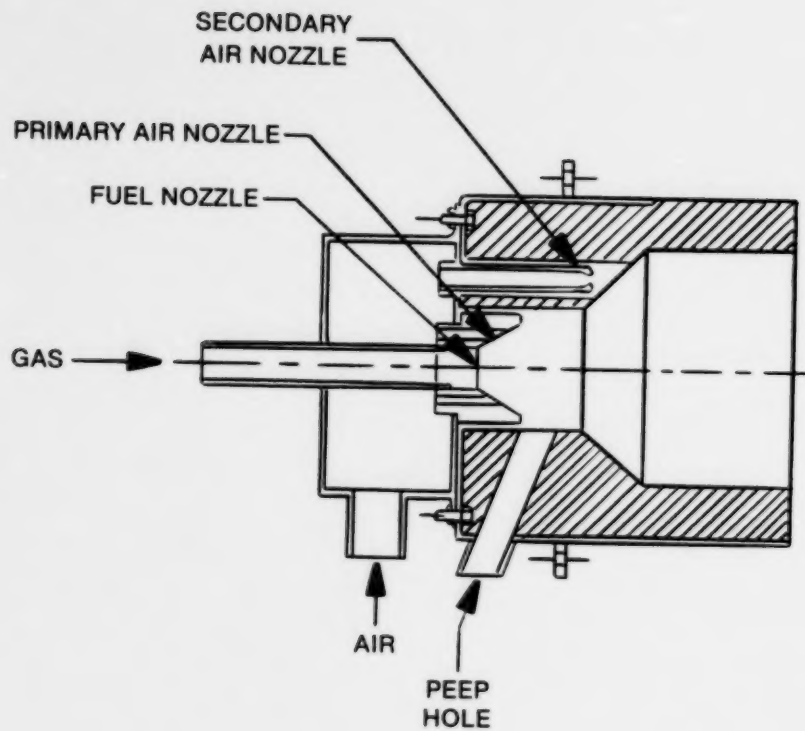
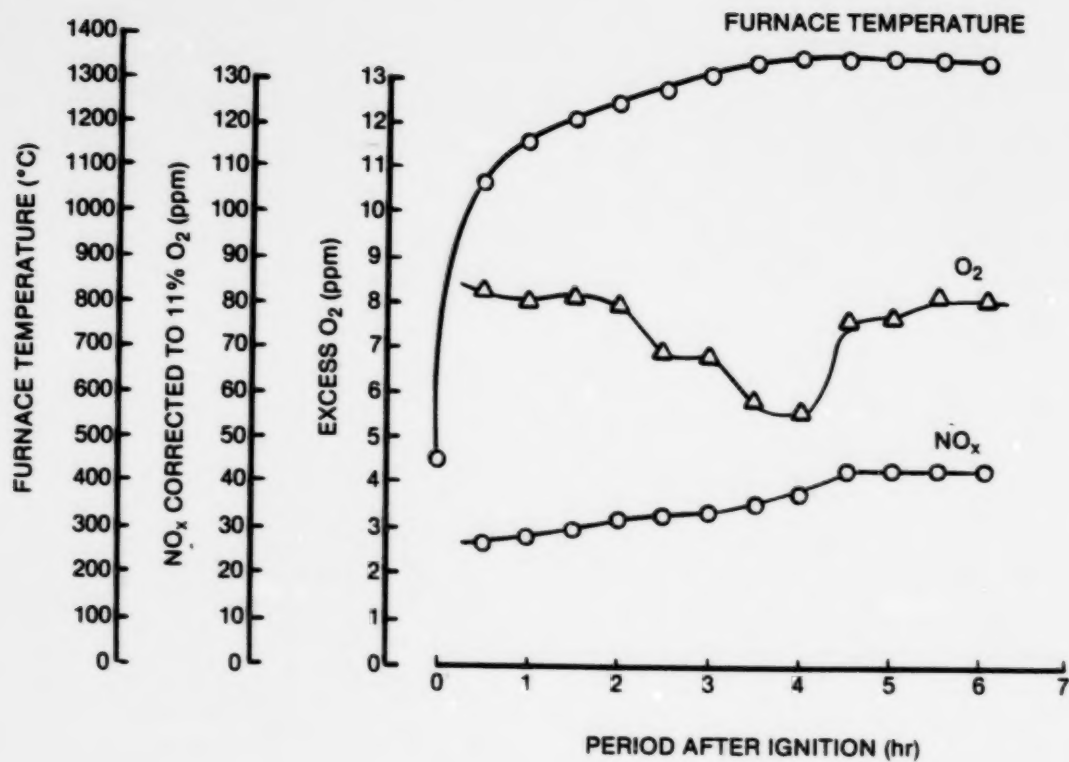


Figure 2-56 TS Burner.





(Fuel: city gas; calorific value: 5000 kcal/Nm<sup>3</sup>,  
number of burners: 6 units)

**Figure 2-57** NO<sub>x</sub> Emission Level of the TS Burner in a Batch Forging Furnace with a Capacity of 20 t/charge.

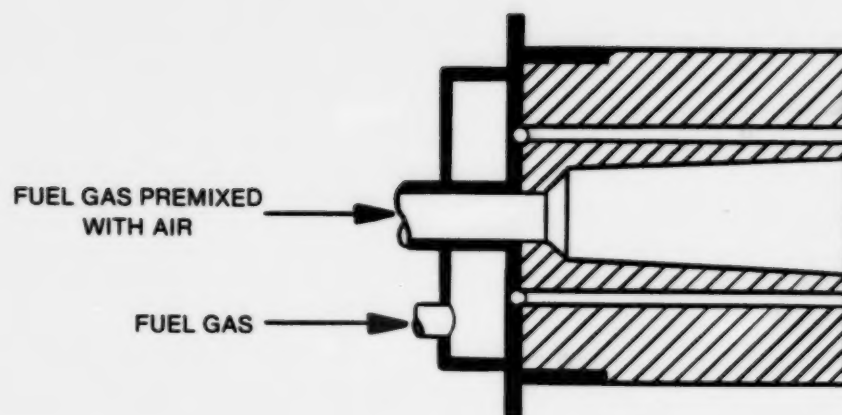
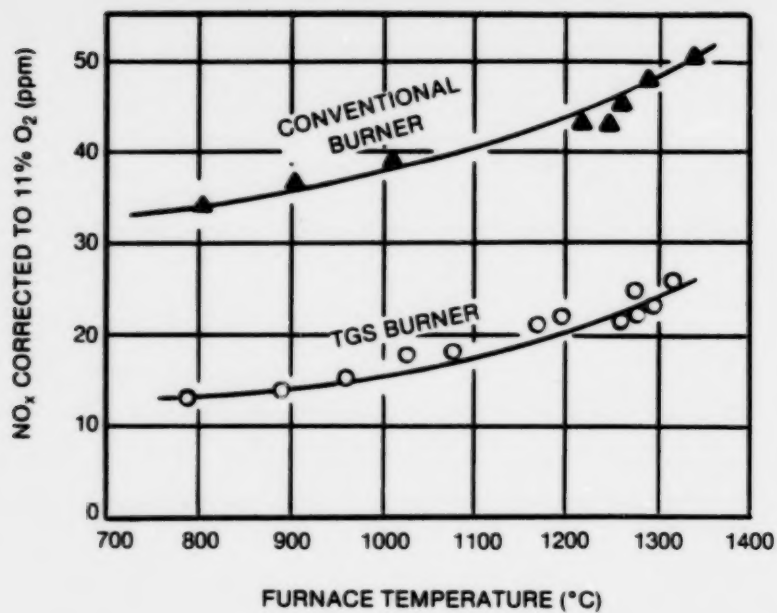


**Figure 2-58**      **Schematic of TGS Burner.**



(Fuel: city gas; calorific value: 5000 kcal/Nm<sup>3</sup>; number of burners: 4 units; thermal input:  $2.4 \times 10^5$  kcal/hr)

**Figure 2-59** NO<sub>x</sub> Reduction Effects of TGS Burner in a Batch Forging Furnace with a Capacity of 2t/charge.

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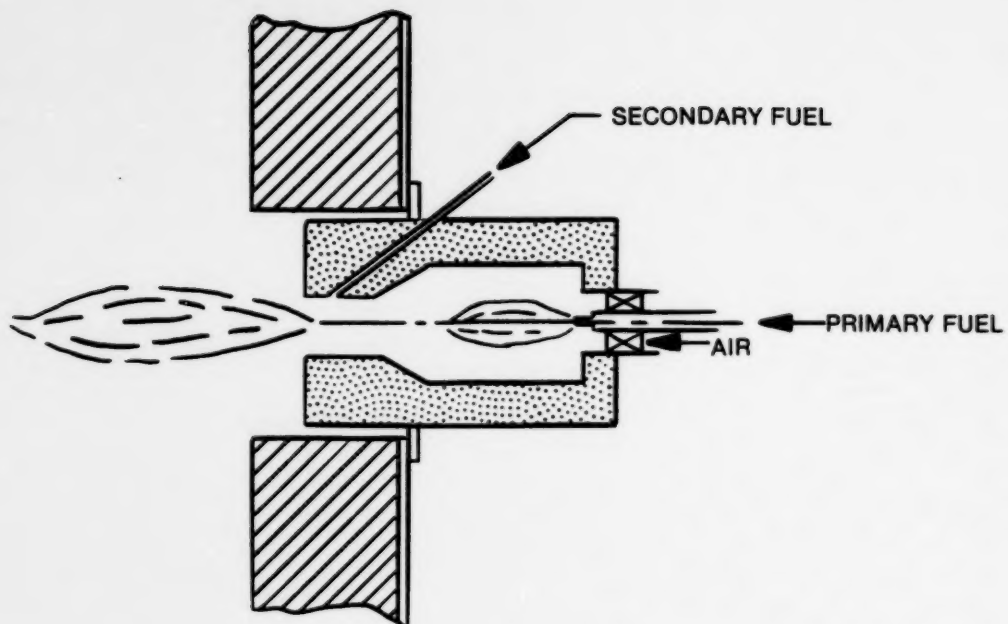
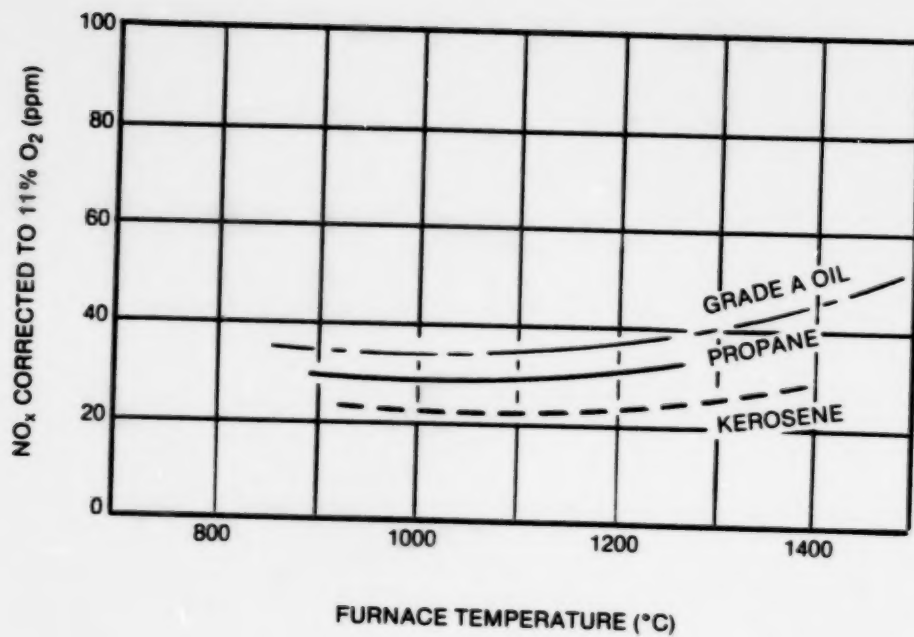


Figure 2-60 Schematic of TZ Burner (Daido Sanso).



(Total emission factor: 1.1; thermal input:  $1.0 \times 10^5$  -  $1.5 \times 10^5$  kcal/hr)

**Figure 2-61** **NO<sub>x</sub> Emission Levels with the TZ Burner.**

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### 2.7.6 Off-Stoichiometric-Combustion Burners

This type of burner first produces fuel-rich and fuel-lean flames both of which have low  $\text{NO}_x$  concentrations. The two flames are then mixed for complete combustion.

Figure 2-62 shows the DLS burner developed by Osaka Gas Company for gas-firing metal-heating furnaces. Its performance is shown in Figure 2-63. Compared with the TS burner (Figures 2-56 and 2-57), the fuel gas in the DLS burner is burned with much less excess  $\text{O}_2$ , and  $\text{NO}_x$  concentrations are almost constant during the operation period.

Figures 2-64 and 2-65 show the improved smokeless PM burner developed by MHI, and its performance. Recirculated flue gas is injected between the air-rich and fuel-rich flames to retard the mixing of the flames, thus causing greater  $\text{NO}_x$  reduction. Particulates, as well as  $\text{NO}_x$ , can be reduced by this burner.

Off-stoichiometric combustion can be attained by a special arrangement of the fuel injection holes in a burner. Figure 2-66 shows such an arrangement in the burner developed by the Volcano Company. The larger holes produce the fuel-rich flame while the smaller holes produce the fuel-lean flame.

Figure 2-67 shows the I-type throat in the dual-air register burner developed by Babcock Hitachi, Ltd. (Section 2.3). From 25-40% of the combustion air is fed through the grooved parts while the rest is fed through the circular part to achieve the off-stoichiometric combustion. The effect of the I-type throat using the off-stoichiometric-combustion type atomizer with an OSC tip is shown in Figure 2-68.

### 2.7.7 Water-Injection Burner

Water-injection burners have been used extensively in Japan because they reduce  $\text{NO}_x$  by lowering the flame temperature and, to some extent, produce effects similar to emulsified oil (Section 2.8.4).



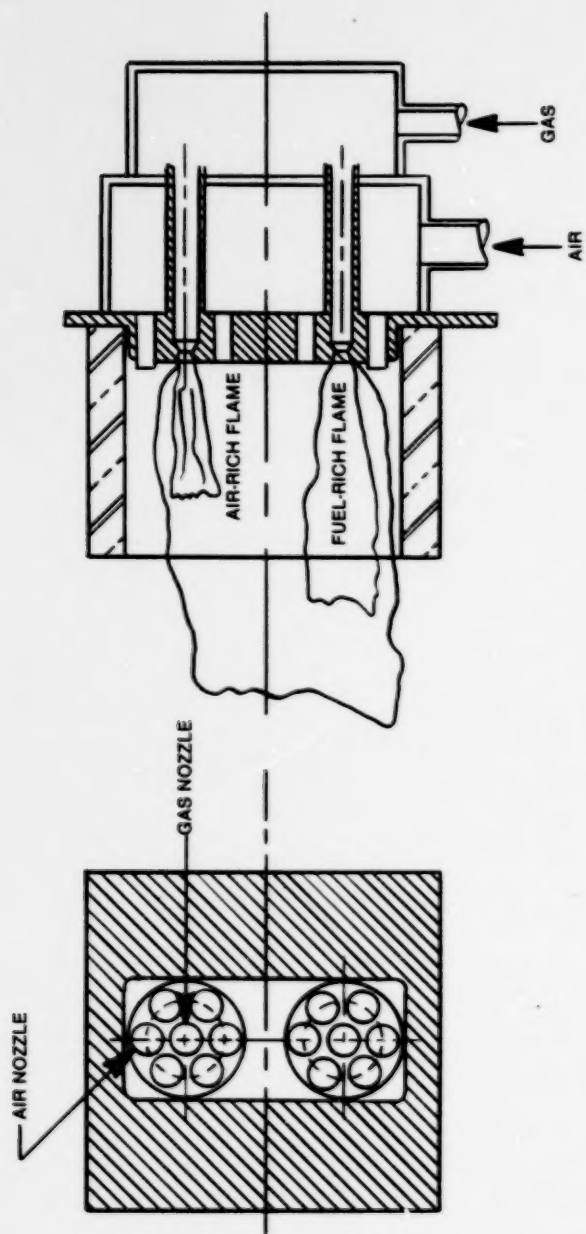
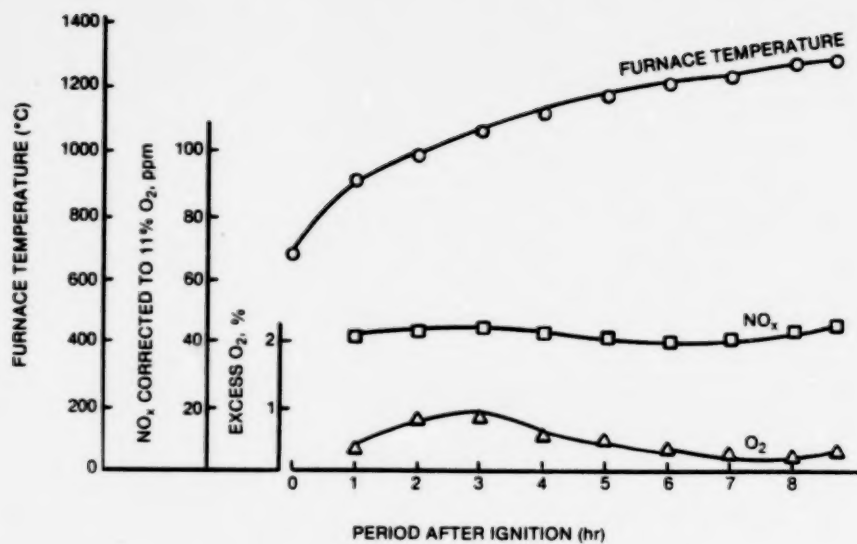


Figure 2-82 Schematic of the DLS Burner (Osaka Gas).



(Fuel: city gas, calorific value: 5000 kcal/Nm<sup>3</sup>)

**Figure 2-83** NO<sub>x</sub> Emission Levels with the DLS Burner in a Batch Forging Furnace with a Capacity of 2t/charge.

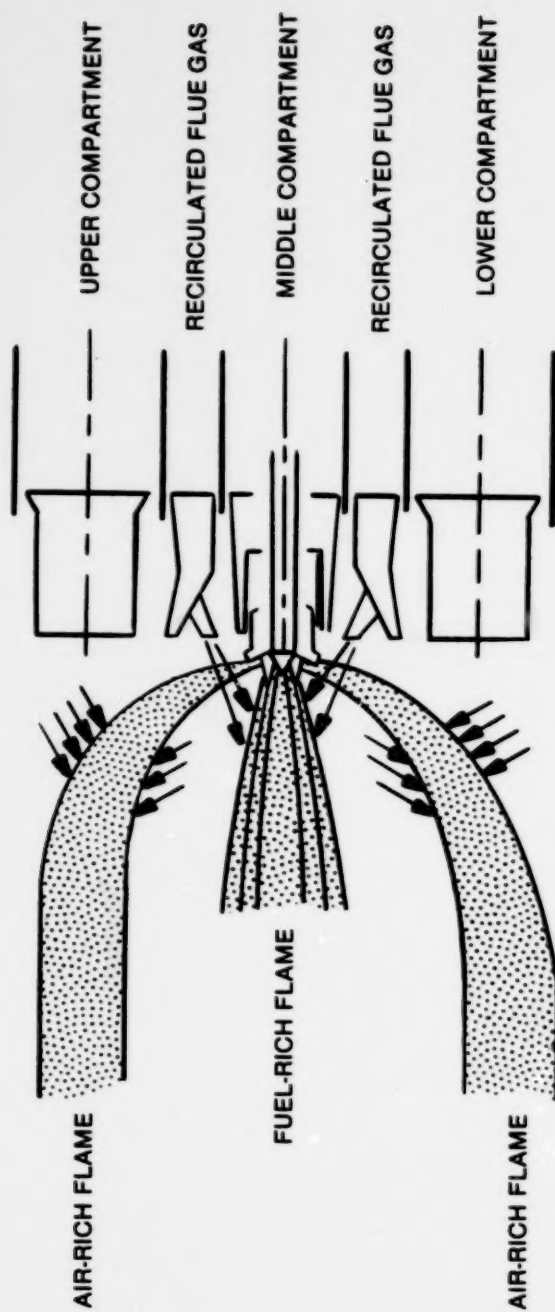
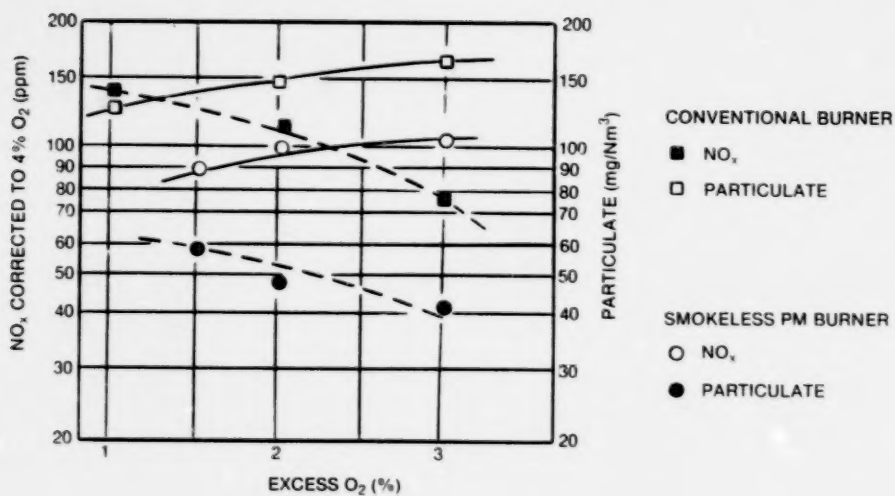


Figure 2-64 Smokeless PM Burner (MHI).



(Fuel: grade B heavy fuel oil; nitrogen content: 0.13%; fire air: about 5%; recirculated flue gas including flue-gas recirculation: 10%)

Figure 2-65 NO<sub>x</sub> and Particulate Reduction with the Smokeless PM Burner.

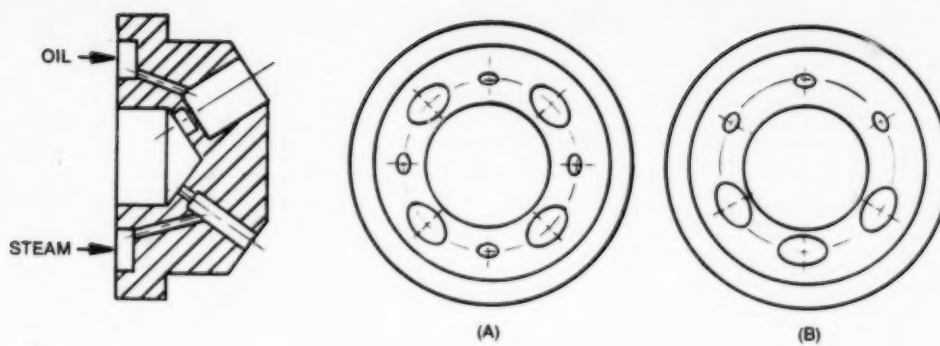


**Figure 2-66** Atomizing Nozzles in the Off-stoichiometric-combustion Low- $\text{NO}_x$  Burner for Oil (Volcano Co.).

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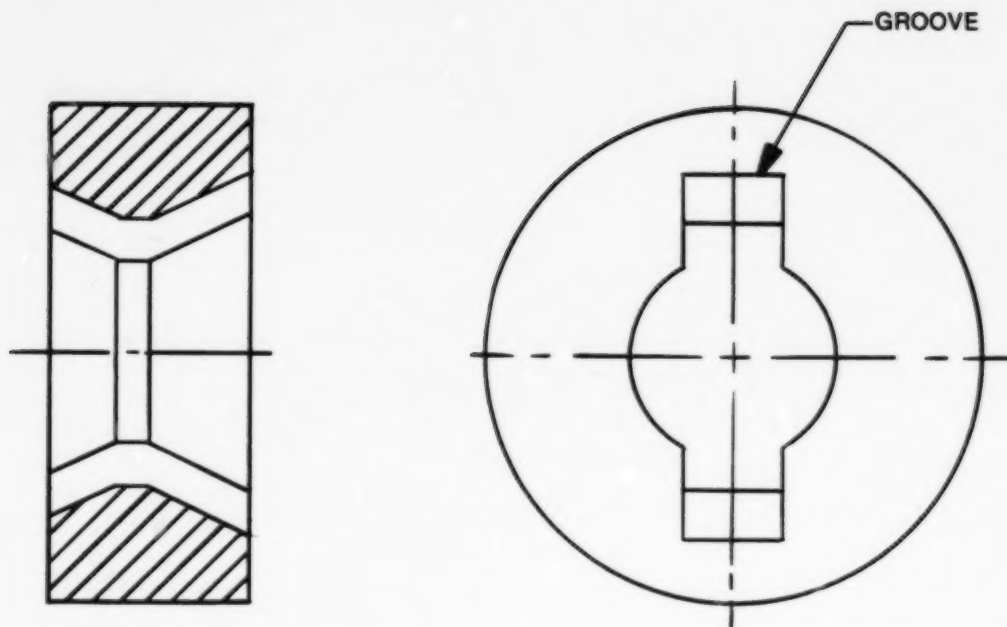
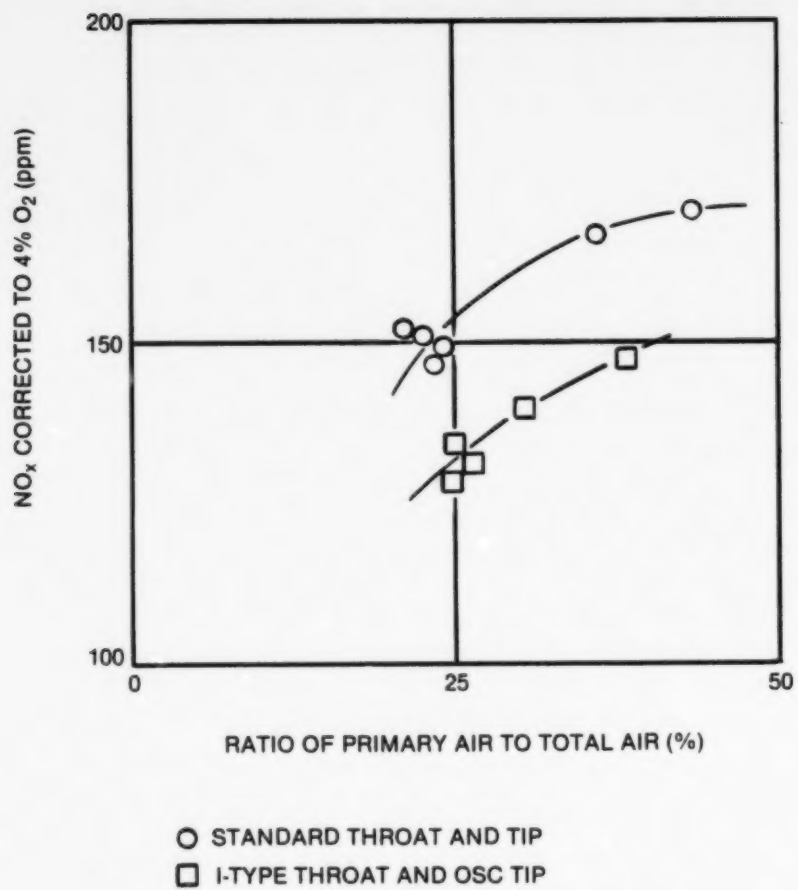


**Figure 2-67 I-Type Throat in the Dual-Air Register Burner.**

70A2581



(Fuel: grade C oil; thermal input:  $3.4 \times 10^5$  kcal/hr)

**Figure 2-68** NO<sub>x</sub> Reduction of the OSC Burner with I-Type Throat in a Watertube Boiler (15 t/hr).



Burner tips for water injection, developed by Asahi Chemical Industry jointly with Nippon Plant Engineering Co., are shown in Figure 2-69. Oil and water are ejected with steam in different ways with various types of tips. The type-C tip generally gives the best results, reducing both  $\text{NO}_x$  and particulates as shown in Figure 2-70. Similar types of tips also are used by Osaka Gas Co.

The JSR burner, developed by the Japan Synthetic Rubber Company, injects water and oil from separate holes as shown in Figure 2-71.  $\text{NO}_x$  reduction with the burner is shown in Figure 2-72. The  $\text{NO}_x$  reduction is caused not only by the lowering of the flame temperature which reduces thermal  $\text{NO}_x$ , but also by the atmosphere produced by the reaction of water and oil which reduces the fuel  $\text{NO}_x$ .

The UN burner, shown in Figure 2-73, injects water into the atomizing air pressurized at 1 to 2  $\text{kg/cm}^2$ . The relationship between the water-injected burner and  $\text{NO}_x$  emissions is shown in Figure 2-74. In addition, water injection reduces soot formation and thus enables low excess air combustion, sometimes resulting in energy savings.

#### 2.7.8 Combination Burner

There are several low- $\text{NO}_x$  burners which use a combination of the above  $\text{NO}_x$  reduction principles. For example, the SRG burner (Figure 2-75), developed by Nippon Furnace Kogyo Kaisha, Ltd., applies two-stage combustion and self recirculation of flue gas. The self recirculation is attained by the Coanda effect of the high-velocity combustion gas. These burners have been used mainly for oil- and gas-fired furnaces at chemical plants and refineries.  $\text{NO}_x$  levels produced by the SRG burner, in comparison with conventional Tandem burners, are shown in Figure 2-76.

The CVS Voltmetric burner, shown in Figure 2-77, was developed by Chugairo Kogyo and is based on a similar  $\text{NO}_x$  reduction principle.

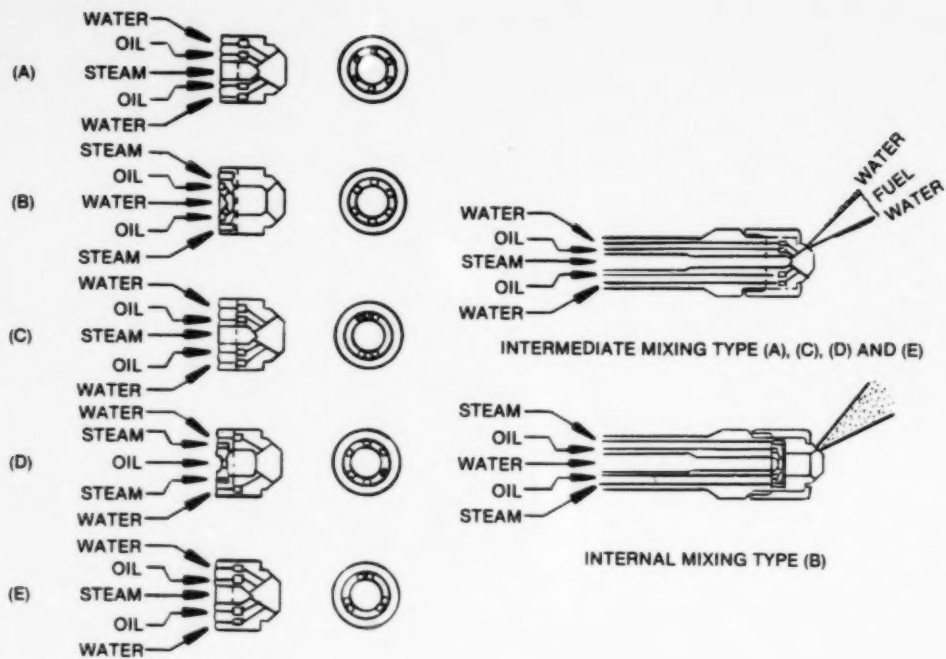
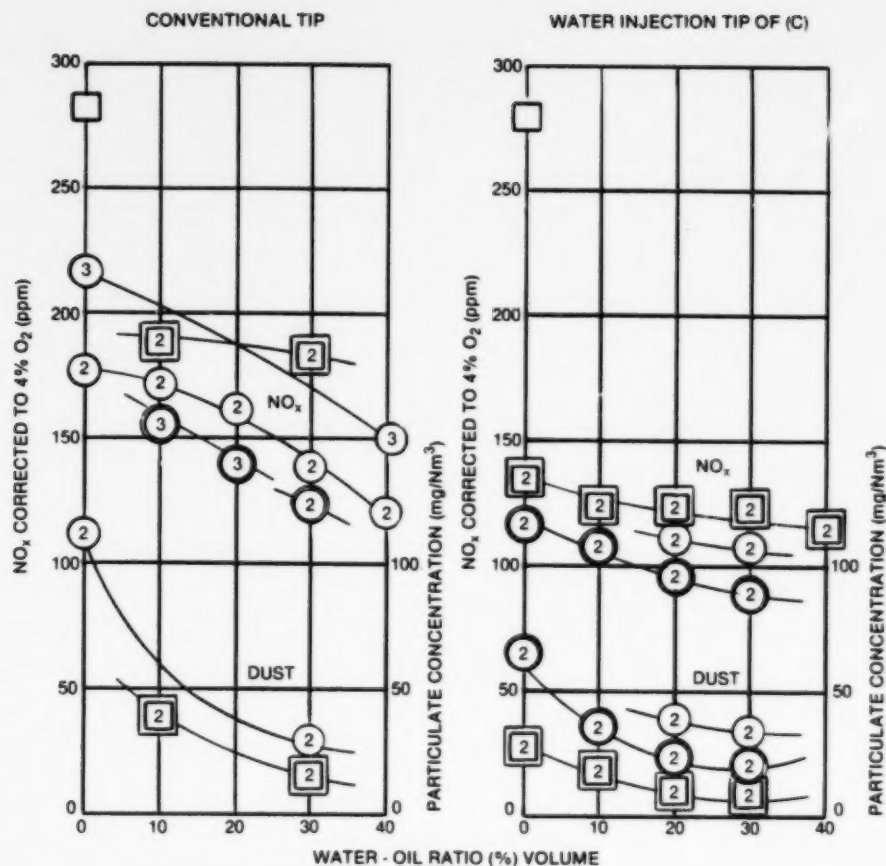


Figure 2-69 Atomizer Tips and Distribution of Water Particles.



(Fuel: grade C oil; fuel flow rate: 11 t/h; number of burners: 9 units;  
firing type: front firing; combustion air temperature: 115°C)

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Figure 2-70 NO<sub>x</sub> Reduction by Water-Injection Atomizer Tip in a Boiler with a Capacity of 162 t/hr.

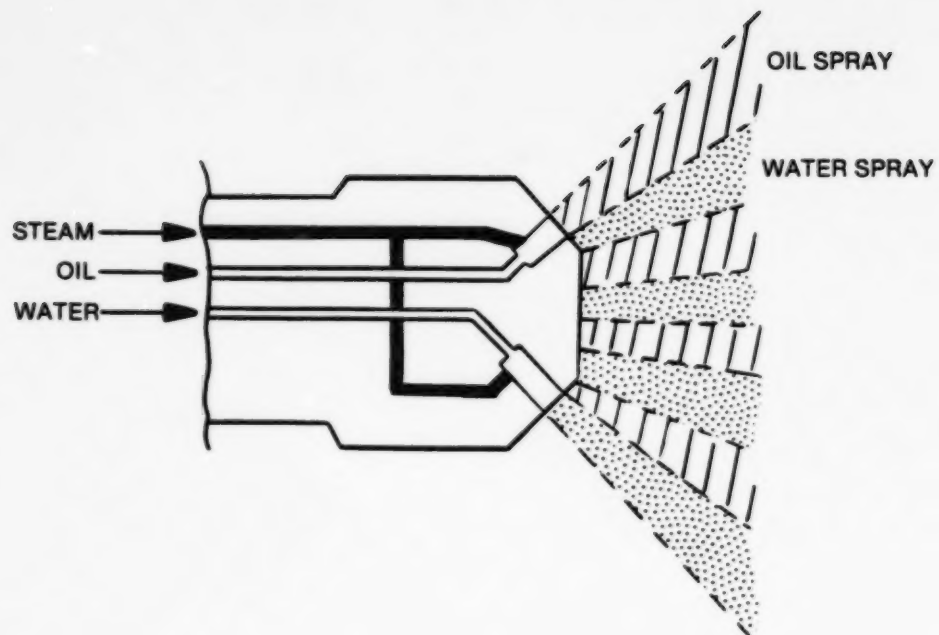
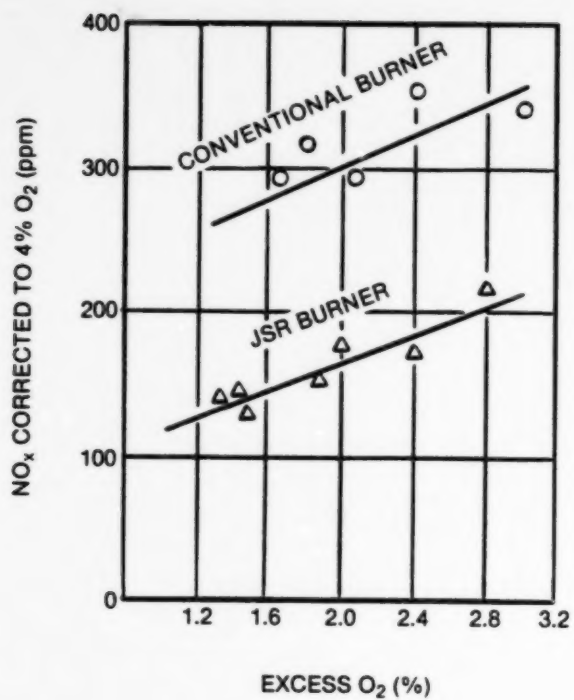


**Figure 2-71     Schematic of JSR Burner (Japan Synthetic Rubber).**



(Fuel: grade C oil; firing type: front firing)

**Figure 2-72** NO<sub>x</sub> Reduction with JSR Burner in a Boiler with a Capacity of 130 t/hr.

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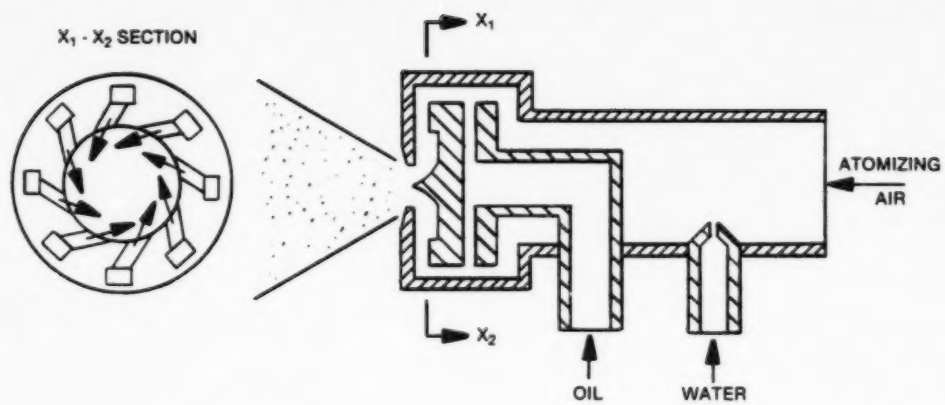


Figure 2-73 Schematic of UN Burner.

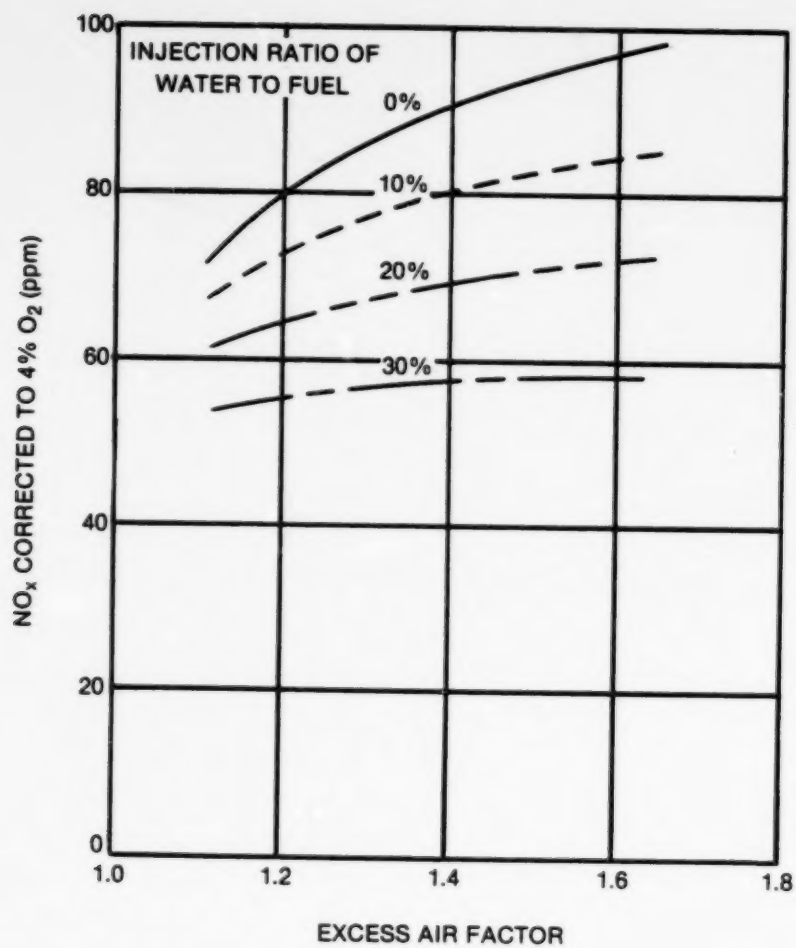


Figure 2-74 NO<sub>x</sub> Emission Levels with UN Burner.



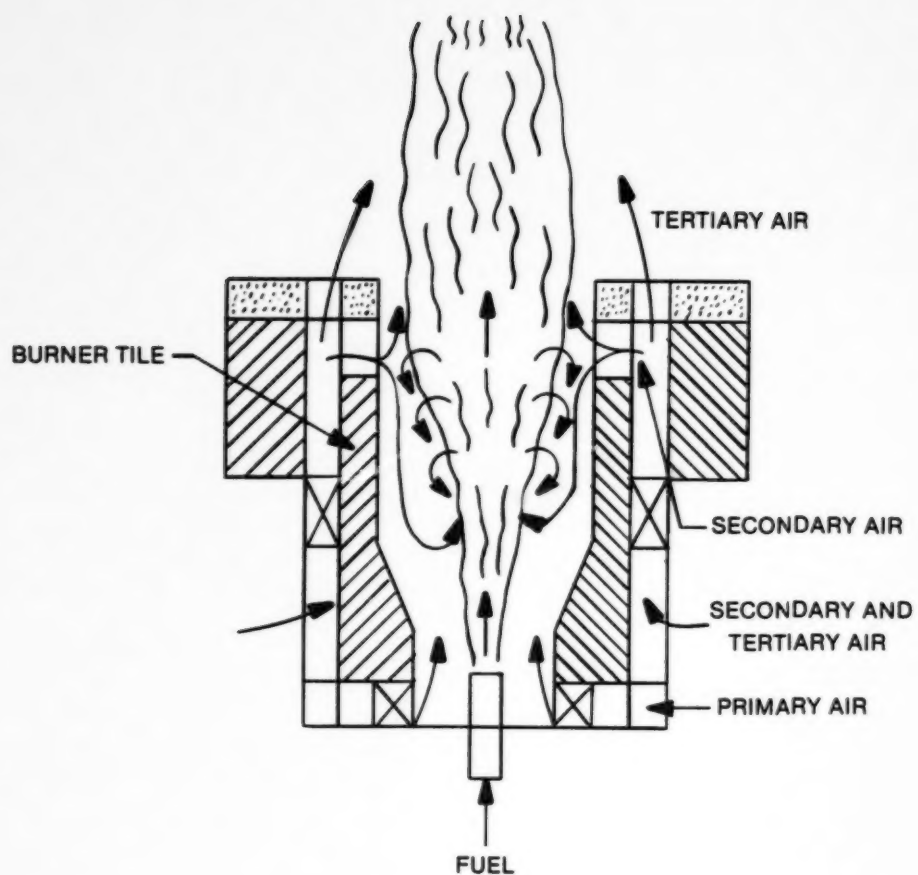


**Figure 2-75 Schematic of SRG Burner. (Nippon Furnace Kogyo Kaisha)**

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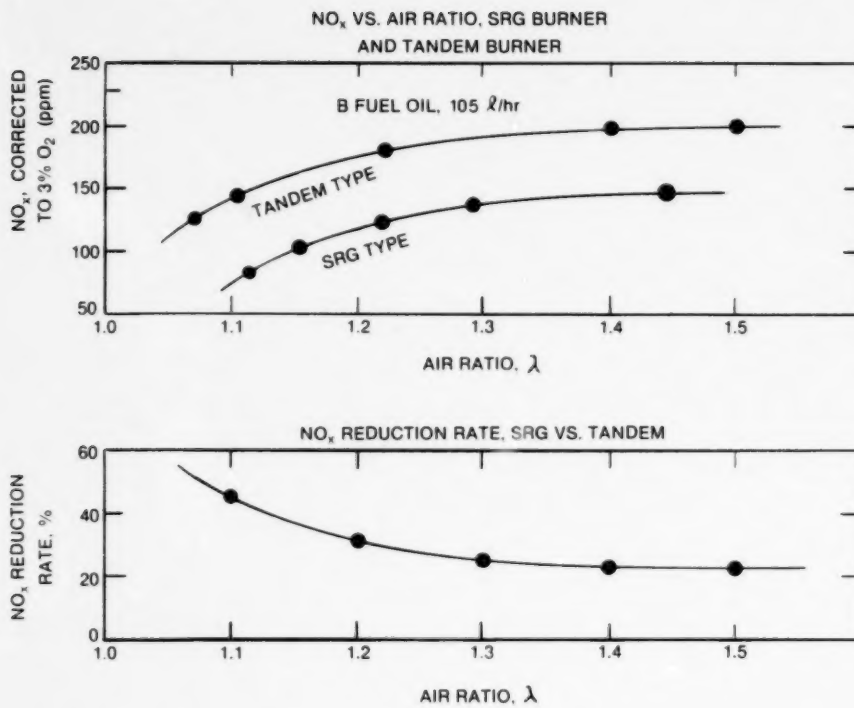


**Figure 2-76** Effect of SRG Burner on NO<sub>x</sub> Reduction.

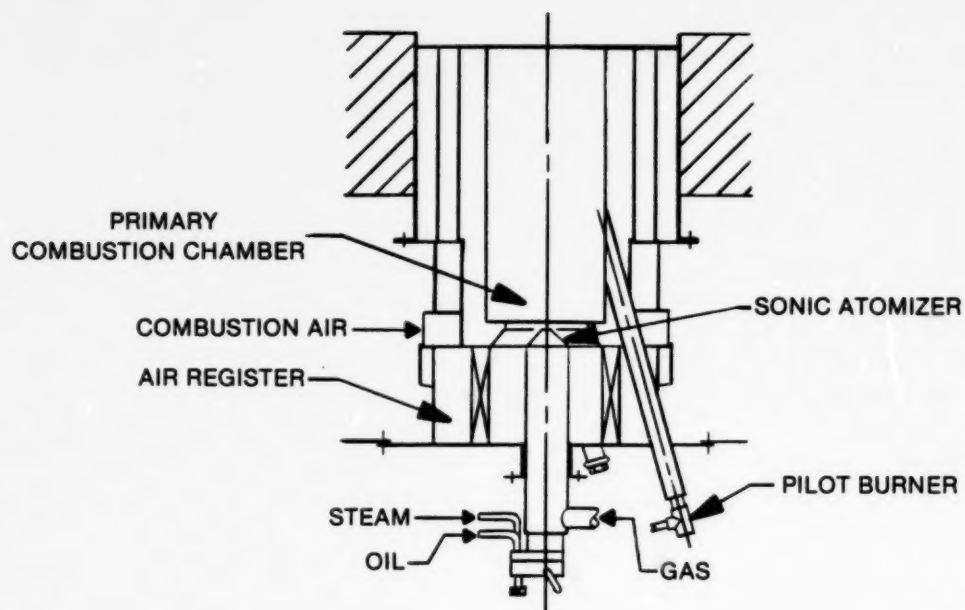


**Figure 2-77** Schematic of CVS Voltmetric Burner (Chugairo Kogyo).

Figure 2-78 shows the TCG burner developed by Osaka Gas Co. jointly with Hirakawa Tekko Co. Self recirculation of combustion gas is achieved by the high-velocity secondary fuel, while off-stoichiometric combustion is attained by separate injection of fuels.

The HLN burner developed by Hosoyama Neki Co. is shown in Figure 2-79. The burner applies flue gas recirculation and two-stage combustion.  $\text{NO}_x$  levels with the burner are shown in Figure 2-80.

## 2.8 COMBUSTION MODIFICATION FOR SPECIAL $\text{NO}_x$ SOURCES AND FUELS

### 2.8.1 Refuse Incinerators (14)

Flue gas from refuse incinerators usually contains about 150 ppm  $\text{NO}_x$  (corrected to 12%  $\text{O}_2$ ). A large portion (70-80%) of the  $\text{NO}_x$  is derived from nitrogen compounds in the refuse. The conversion ratio of fuel nitrogen to  $\text{NO}_x$  is considered to be 8-12% under normal incineration conditions. In a low excess air incinerator, a conversion ratio of 8% was reported.

$\text{NO}_x$  conversion characteristics for refuse incineration are similar to those of oil and coal burning for the following reasons:

- (1) Furnace temperatures do not affect the conversion ratio appreciably.
- (2) Types of nitrogen compounds in the refuse do not greatly influence the conversion ratio.
- (3) Generally, the larger the nitrogen content, the smaller the conversion ratio. The conversion ratio, however, essentially stays constant above a certain nitrogen content.
- (4) The conversion ratio increases with the excess air factor.

Based on these characteristics, staged combustion is considered most effective for abatement of  $\text{NO}_x$  abatement in incinerator flue gas. Reducing gases such as  $\text{NH}_3$ , hydrocarbons, and HCN, formed at the first stage in the

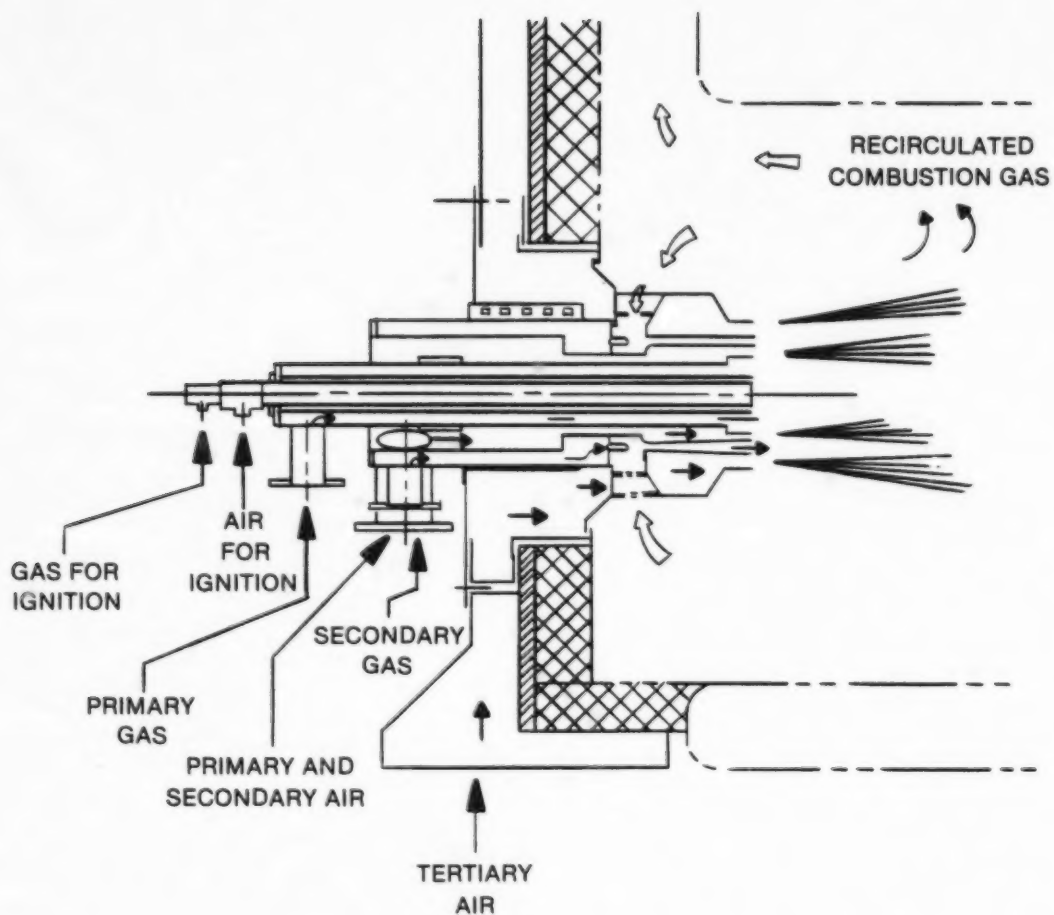


**Figure 2-78 Schematic of TCG Burner (Osaka Gas/Hirakawa Tekko).**

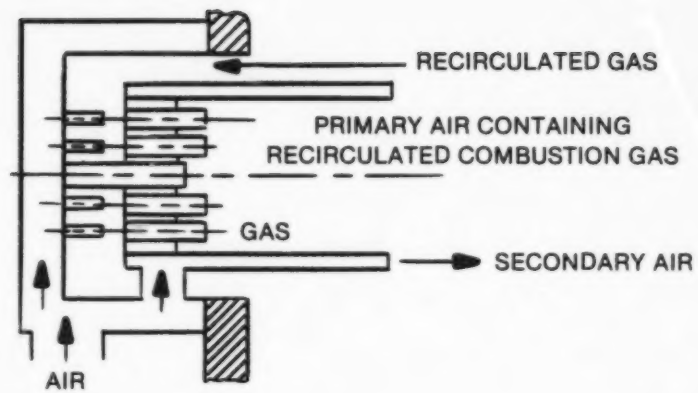
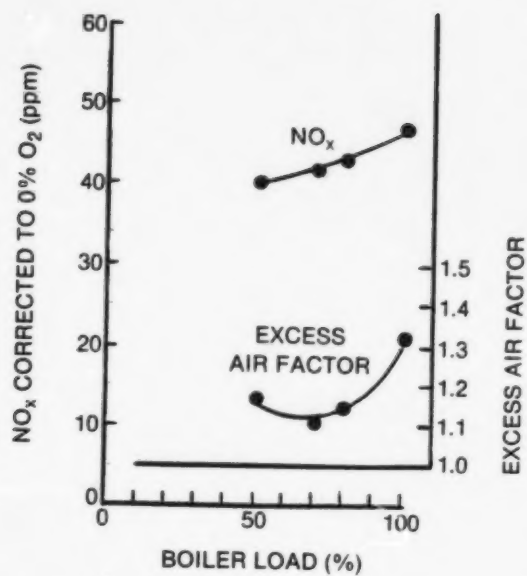


**Figure 2-79 Schematic of HLN Burner (Hosoyama Neki).**



(Fuel: city gas; calorific value: 5000 kcal/h)

**Figure 2-80** NO<sub>x</sub> Emission Level with HLN Burner in a Boiler with a Capacity of 1.3 t/hr.

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reducing atmosphere, decompose  $\text{NO}_x$  and keep the  $\text{NO}_x$  conversion ratio as low as 5%.

Problems with staged combustion and modifications to remedy them are shown below:

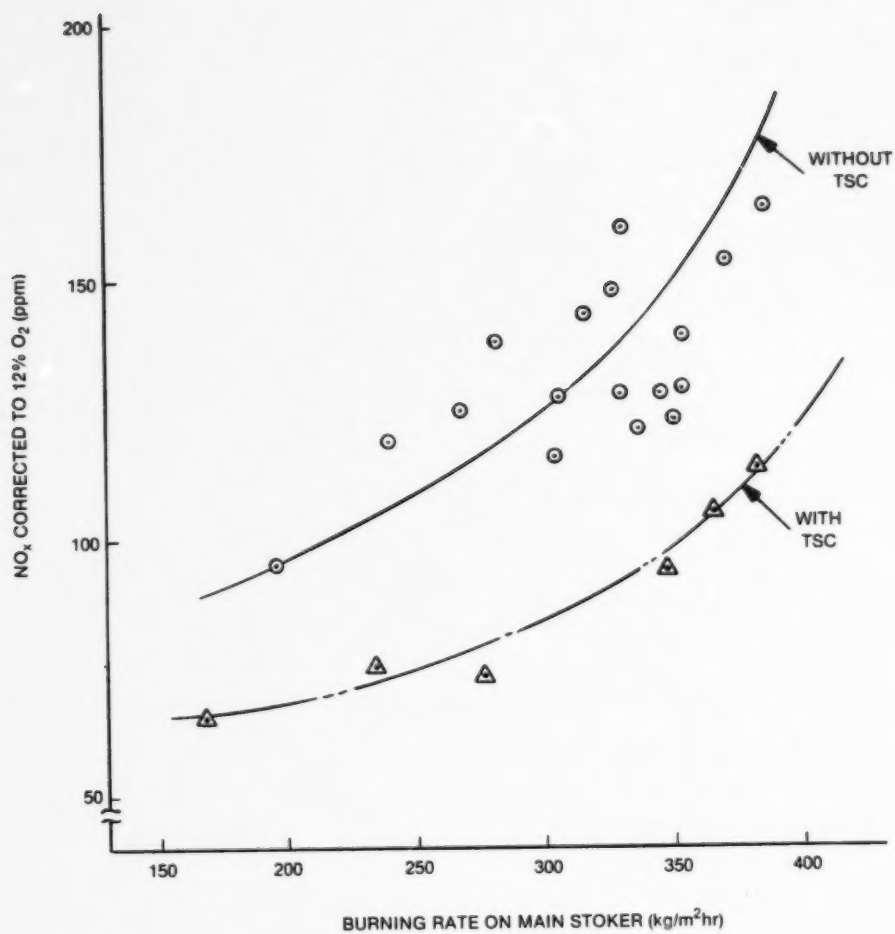
| <u>Problems</u>                | <u>Modifications</u>                                           |
|--------------------------------|----------------------------------------------------------------|
| Increase of unburned carbon    | Increase of stoker area<br>Application of after-burning system |
| Control of furnace temperature | Flue gas recirculation<br>Water injection<br>Steam injection   |

By making these modifications to two-stage combustion,  $\text{NO}_x$  emissions below 120 ppm (corrected to 12%  $\text{O}_2$ ) are achieved, as shown in Figure 2-81. This emission level more than meets the emission standard of 250 ppm  $\text{NO}_x$  (corrected to 12%  $\text{O}_2$ ) for a new incinerator.

#### 2.8.2 Cement Kilns (15)

Rotary kilns for cement production usually produce a flue gas containing a high concentration of  $\text{NO}_x$ —400–1,000 ppm—even with oil firing. This is due to the long retention time of the gas at temperatures of 1000–1550°C and the presence of a large excess of air. A new NSP kiln with suspension preheaters and a gas generator (GG) or a flash furnace (FF) (Figures 2-82 and 2-83) has been developed and used in Japan. It has a high production efficiency and produces  $\text{NO}_x$  emissions below 200 ppm; the emission standard for new kilns is 250 ppm (corrected to 10%  $\text{O}_2$ ).

A conventional rotary kiln uses all of the fuel from a burner located at one end of the kiln to produce a wide range of high temperatures (1000–1550°C). This assures the decomposition of calcium carbonate and the reaction of lime with clay and other raw materials to form the cement clinker. With the new types of kilns equipped with GG or FF systems, one half of the fuel is injected into the gas generator or flash furnace (calciner). The furnace is installed at the opposite end of the kiln to assure calcination of the feed



(Refuse feed rate: 150 t/24hr)

Figure 2-81 NO<sub>x</sub> Reduction by Two-Stage Combustion in a Refuse Incinerator.

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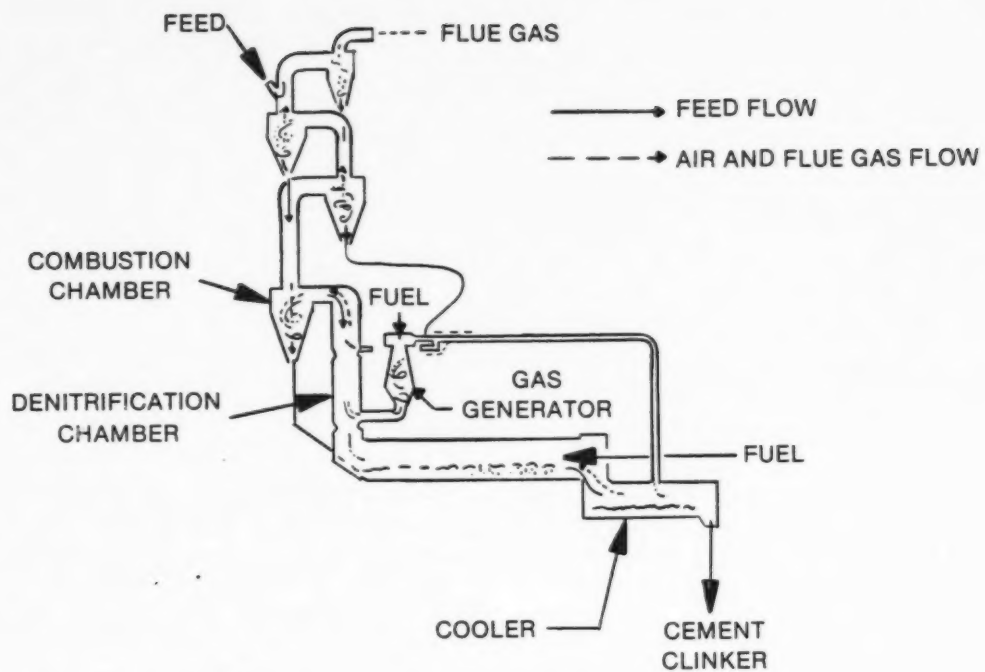


**Figure 2-82** Flow Diagram of the GG Process Used in Cement Kilns.

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and decomposition of the calcium carbonate at around 1,000°C. NO<sub>x</sub> formation in the kiln is substantially lowered by the reduced heat load. With the GG system, it is possible to use the reducing gas to remove NO<sub>x</sub> formed in the denitrification chamber. The reducing gas is burned by the hot air leaving the cement clinker cooler. NO<sub>x</sub> concentrations can be reduced below 150 ppm (corrected to 10% O<sub>2</sub>), easily meeting the emission standard.

Use of coal instead of oil with the GG system does not cause a substantial increase in NO<sub>x</sub> since NO<sub>x</sub> can be removed in the denitrification chamber by the reducing gas.

Mitsui Mining Co. has modified the FF system originally developed for oil firing for use with coal, as shown in Figure 2-83. The major modifications are as follows (16):

- (1) A larger calciner (furnace) is used to ensure complete coal combustion.
- (2) A low-pressure-drop suspension preheater is used to deal with the increase in gas volume caused by the use of coal rather than oil.
- (3) The feed is introduced into the calciner from both the bottom and the side to ensure better calcination and the correct combustion temperature for NO<sub>x</sub> reduction.

### 2.8.3 Glass Melting Furnaces

Glass melting furnaces burning gas or oil used to emit high levels of NO<sub>x</sub> (above 50 ppm) due to: 1) high furnace temperatures of approximately 1,600°C, 2) relatively long gas-retention times needed to ensure the melting and clarification of the glass, and 3) the high O<sub>2</sub> concentration of the gas. When sodium nitrate is used as a feed to promote clarification, the NO<sub>x</sub> concentration in the flue gas commonly exceeds 2,000 ppm. The use of nitrate, however, has almost been eliminated in Japan in order to reduce NO<sub>x</sub> emissions.

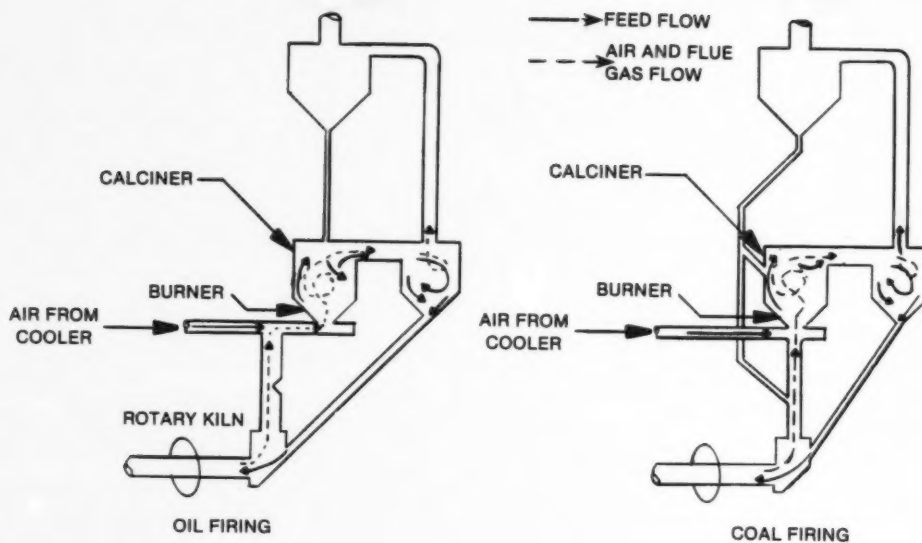


Figure 2-83 The FF System Used in Both Oil and Coal-fired Cement Kilns.

In furnaces not using nitrate, virtually all of the  $\text{NO}_x$  present in the flue gas is thermal  $\text{NO}_x$ . Using the following measures, this thermal  $\text{NO}_x$  is reduced in much the same manner as it is in other oil- or gas-fired industrial furnaces.

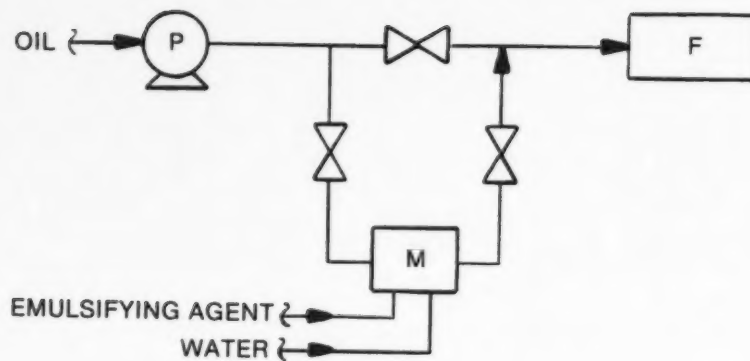
- (1) Suppression of excessively high temperatures
- (2) Prevention of air leakage
- (3) Application of low excess air combustion
- (4) Strict control of  $\text{O}_2$  in flue gas using oxygen sensors

A mild flame with a slow reaction is considered an effective method of  $\text{NO}_x$  abatement for these furnaces. For oil-fired furnaces, the atomizer has been changed from an air to an oil-pressure type. An oil-pressure atomizer that produces a plane flame shape has been developed by the Asahi Glass Company for  $\text{NO}_x$  abatement purposes (17). The plane flame shape is reduced by the slit in the atomizer tip. With the combination of this atomizer and an adequately shaped port, a 40%  $\text{NO}_x$  reduction can be achieved.

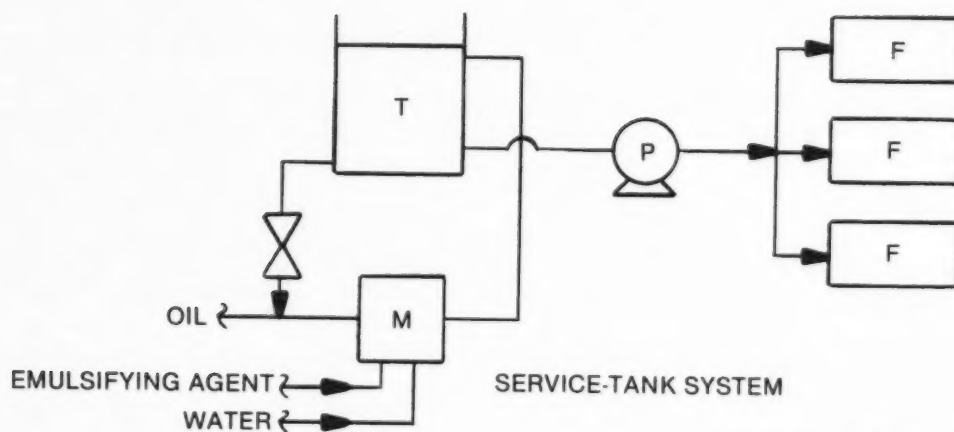
#### 2.8.4 Use of Emulsified Oil for Small Boilers

Emulsified oil (oil-water emulsion) has been used as an efficient method of  $\text{NO}_x$  abatement for small boilers. In some cases emulsified oil also may be effective for saving energy because it allows a reduction in excess air without causing incomplete combustion.

Many companies have developed systems for producing emulsified oil. These systems may be divided into two categories, as shown in Figure 2-84. The line blending system generally is more advantageous than the service tank system because of its simplicity. On the other hand, the service tank system is compatible with many types of combustion equipment, although pump cavitation may be an operational problem with this system. Different types of emulsifying agents, in concentrations of 0.1 to 0.2%, are used with various types of boiler fuels.



LINE BLENDING SYSTEM



SERVICE-TANK SYSTEM

P: PUMP  
M: MIXER  
T: TANK  
F: FURNACE SYSTEMS

Figure 2-84 Emulsified Oil Production Systems.



Upon combustion of the emulsified oil, the atomized oil droplets are separated into very small particles by sudden expansion of the water contained in the emulsion. This increases the contact area for the oil and air, thus increasing the combustion rate, and reducing thermal  $\text{NO}_x$  formation. Since water and steam can be used to slow the formation of soot as shown in Figure 2-85, excess air can be further reduced as shown in Figure 2-86 (18). Therefore, an increase in thermal efficiency may be expected when using emulsified oil for small boilers. The reducing atmosphere formed by the reaction of the water and fuel promotes the reduction of  $\text{NO}_x$ . Injection, agitation, and static mixers all have been used to produce emulsified oil.

#### 2.8.5 Special Fuels and Processes

##### Coal Oil Mixture (COM)

COM is a slurry composed of equal amounts of oil and pulverized coal. In Japan, EPDC and major boiler manufacturers have conducted studies of COM, because the slurry can reduce oil consumption without the handling problems inherent in coal use. The combustion properties of COM compared with those of oil are as follows.

- (1) The ignition characteristics of COM are similar to those of oil, but the atomized particles are often finer.
- (2) With COM the flame becomes longer; oil burns initially, followed by the combustion of volatile matter, and then by the combustion of the fixed carbon of the coal.
- (3) The flame temperature with COM-firing is about equal to that for oil firing.
- (4) The COM burning rate is slower which means that a larger amount of excess air is required. Because of this, the  $\text{NO}_x$  concentration becomes higher.

Because of COM's higher nitrogen content compared to oil, staged combustion is more effective than flue gas recirculation for  $\text{NO}_x$  abatement purposes.  $\text{NO}_x$  concentrations below 200 ppm are achieved by staged combustion.

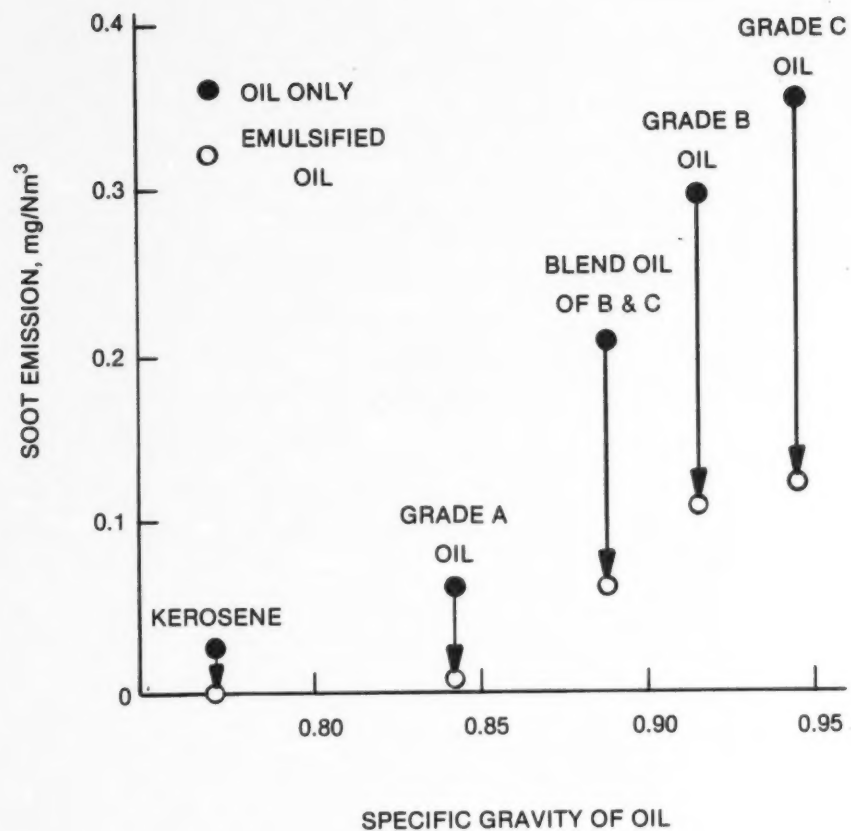
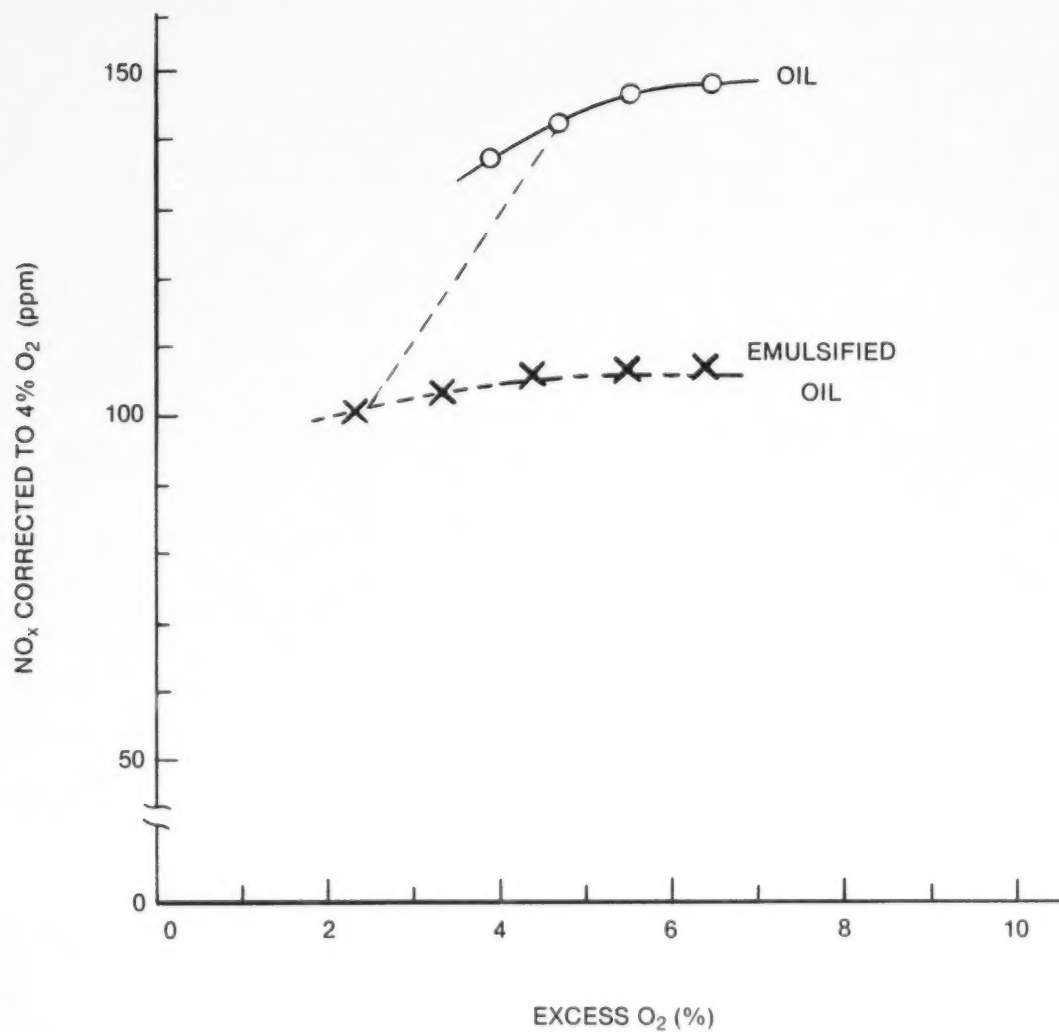


Figure 2-85 Reduction of Soot Emissions by Emulsified Oil.



(Fuel: grade C oil, water mixing ratio: 30%)

**Figure 2-86** NO<sub>x</sub> Reduction By Emulsified Oil in a Water Tube Boiler with a Capacity of 12 t/h.

### Methanol

A feasibility study on the use of methanol by utility boilers has been conducted (19). Combustion tests using a small test furnace produced  $\text{NO}_x$  emissions below 30 ppm under normal conditions and of about 20 ppm when flue gas recirculation was applied.

### Catalytic Combustion

Basic studies on catalytic combustion of gaseous fuels also have been conducted. Catalytic combustion has the following advantages.

- (1) Low-temperature combustion is possible, resulting in low  $\text{NO}_x$  concentrations.
- (2) A wide range of excess air factors can be used without affecting the flame stability.
- (3) Uniform temperature and composition of the combustion gas can be obtained thus avoiding local overheating and formation of high  $\text{NO}_x$  concentrations which occur during conventional combustion.

One test indicated that  $\text{NO}_x$  levels below 20 ppm were attained even with a combustion temperature of  $1,600^\circ\text{C}$  and a catalyst. A large volumetric heat release rate was produced without forming unburned species such as CO and hydrocarbons (20).

One disadvantage of catalytic combustion is that the catalyst can be physically unstable if subjected to repeated temperature variations.

### Fluidized Bed Combustion

Fluidized bed combustion (FBC) of coal has the following advantages:

- (1) Low  $\text{SO}_x$  emissions can be achieved by adding limestone or dolomite in the combustion zone.

- (2) Low  $\text{NO}_x$  emissions may be achieved because of the low combustion temperature (around  $1,000^\circ\text{C}$ ).
- (3) Smaller boiler sizes are possible due to a higher heat transfer efficiency and a higher heat release rate in the furnace.
- (4) Low-grade as well as high-grade coals may be burned.

The Coal Mining Research Center, jointly with EPDC, KHI, and Babcock Hitachi, constructed a 5 MW equivalent atmospheric FBC pilot plant at EPDC's Wakamatsu Station. The plant began operation in April 1981 (21). Preliminary tests using domestic low-sulfur coal (0.2% S and 0.9% N) and limestone indicated that when staged combustion was applied,  $\text{NO}_x$  was reduced to 64 ppm. Construction of a 75 MW demonstration plant will begin in 1983; the plant should be operating by 1985.

A small commercial atmospheric FBC plant owned by the Sumitomo Colliery Akabira Company (10 t/hr steam, 2.5MW equivalent) began operation in April 1980 (22). The furnace burns a low-grade coal (3,050 kcal/kg) recovered from coal-wash water and uses silica sand as the fluidizing agent. The plant, constructed by Babcock Hitachi, is a modification of an oil pulverized coal-fired boiler.  $\text{NO}_x$  concentrations in the flue gas have ranged from 260-350 ppm.

However, fluidized bed combustion has the following disadvantages in Japan:

- (1) There is no land space for disposal of ash containing calcium sulfate, lime, and other materials.
- (2) Although tests have been conducted on a process to separate and regenerate the  $\text{SO}_x$  absorbent, there are both technical and economic problems associated with the process.
- (3)  $\text{SO}_x$  and  $\text{NO}_x$  concentrations in the flue gas may not be low enough to meet the stringent local regulations. In Japan, both FGD and SCR have been applied successfully to coal-fired boilers to reduce  $\text{SO}_x$  and  $\text{NO}_x$  to very low levels.

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### SECTION 3

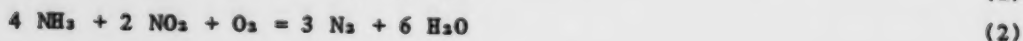
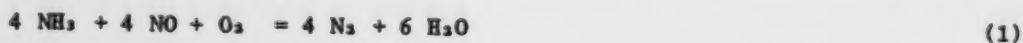
#### SELECTIVE CATALYTIC REDUCTION (SCR) OF NO<sub>x</sub>

##### 3.1 REDUCTION OF NO<sub>x</sub> BY AMMONIA

###### 3.1.1 Basic Reactions

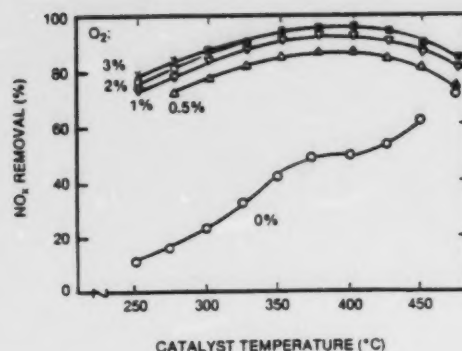
Virtually all of the NO<sub>x</sub> in combustion gases is present in the form of NO, while NO<sub>x</sub> from non-combustion sources, e.g., nitric acid plant tail gas, consists of both NO<sub>2</sub> and NO. Although NO<sub>x</sub> can be reduced to N<sub>2</sub> with the use of reducing gases such as CH<sub>4</sub>, H<sub>2</sub>, and CO, these gases are also readily consumed by reaction with O<sub>2</sub>. NH<sub>3</sub> is a more economical reducing agent for a gas with a high O<sub>2</sub>/NO<sub>x</sub> ratio, because NH<sub>3</sub> selectively reacts with NO<sub>x</sub>.

Since a small amount of O<sub>2</sub> promotes the reaction of NH<sub>3</sub> with NO<sub>x</sub>, the reaction is usually expressed by equations 1 and 2.



Combustion gases usually contain at least one percent O<sub>2</sub>, which is sufficient for the reaction (Figure 3-1).

The optimum temperature for the reactions without a catalyst is 900-1000°C. Above this temperature, a considerable portion of the NH<sub>3</sub> is converted to NO<sub>x</sub>. Below this temperature, the reaction rate is slow. Selective noncatalytic reduction (SNR), the injection of NH<sub>3</sub> into a boiler or furnace at 800-1000°C, has been applied on a commercial scale, but NO<sub>x</sub> removal is usually limited to 30-50% at NH<sub>3</sub>/NO mole ratios of 1-2 (Section 6.2).



(SV: 10,000 hr<sup>-1</sup>; NO<sub>x</sub>: 100 ppm; NH<sub>3</sub>/NO<sub>x</sub>: 1.0)

Figure 3-1 Effect of Oxygen on NO<sub>x</sub> Removal. (1)

Selective catalytic reduction (SCR) uses a catalyst at 150–450°C and achieves 80–90% NO<sub>x</sub> reduction with an NH<sub>3</sub>/NO mole ratio in the range of 0.85–1. Various catalysts are effective in the temperature range of 300–400°C, which is the temperature of utility boiler economizer outlet gas.

### 3.1.2 Problems with SCR

The serious problems encountered in the early stages of SCR development have largely been solved. Catalyst poisoning by SO<sub>x</sub> was solved by substituting base metal catalysts based on TiO<sub>2</sub> for Al<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub>. Catalyst plugging problems in dust-laden gases were eliminated with the use of honeycomb, plate, and tube ("parallel flow") catalyst configurations or parallel flow reactors. Soot blowing is also used to remove dust. Ammonium bisulfate formation occurs when NH<sub>3</sub>, SO<sub>3</sub>, and H<sub>2</sub>O react due to temperatures below 300°C caused by reduced boiler loads. Bisulfate deposits lower catalytic activity. Ammonium bisulfate formation has been prevented by maintaining a gas temperature above 300°C, either by adjustments in economizer efficiency or with a hot gas bypass upstream of the economizer. Economizer energy losses are recovered with an air preheater downstream of the SCR. Ammonium bisulfate tends to deposit in the air preheater. The deposits can be prevented or minimized by maintenance of low levels (<5 ppm) of NH<sub>3</sub> in the reactor outlet gas.

Oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  also occurs with some catalysts, increasing the formation of ammonium bisulfate. Low-oxidation catalysts have been developed to address this problem. Finally, catalyst erosion by fly ash particles has been prevented by maintaining moderate gas velocities, increasing catalyst hardness, and employing the "dummy spacers" described in Section 3.4.

These improvements have increased the reliability and ease of operation of SCR processes, resulting in the construction of over 150 commercial plants. Most have been operated with few problems, although ammonium bisulfate deposition in the air preheater continues to occur at some plants.

Catalyst life in commercial SCR systems varies depending on boiler fuel. For gas- and oil-fired boilers virtually no degradation has been evident after more than 4 years of operation. In July 1982 coal-fired boilers had operated for over 2 years with little catalyst degradation. The actual life of SCR catalysts may be as long as 6-7 years for gas-fired boilers, 5 years for oil-fired boilers, and 3 years for coal-fired boilers.

Disposal of the spent catalysts is considered a potential problem because of the presence of heavy metals. Virtually no catalysts had required replacement at the time this report was written, so there is little experience with spent catalyst disposal. Since catalyst composition is confidential, producers must recycle all of the spent catalysts to recover the heavy metals. For example, titanium producers are expected to recover  $\text{TiO}_2$ . The feasibility of these recovery practices for exported catalysts is uncertain.

### 3.1.3 Major Factors in Catalytic Reaction

Equation 4 shows the relationship between space velocity (SV) and  $\text{NO}_x$  removal rate:

$$\log(1-x) = -k/\text{SV} \quad (4a)$$

where:

$$k = k_0 S_{ap} \quad (4b)$$

$x$  = Reaction ratio ( $\text{NO}_x$  removal ratio).

$k$  = Reaction constant.

$k_0$  = A constant at a given temperature relating to the catalyst property.

$S_{ap}$  = Apparent surface area. The surface area of the catalyst assuming that the catalyst surface is smooth, not porous.

Space velocity is defined as the ratio of the gas volume passing through the catalyst bed per hour to the volume of the catalyst itself.

A smaller SV and a larger  $k$  give a larger  $x$ . A smaller SV implies that a larger amount of catalyst has been used. The reaction constant,  $k$ , is larger with a larger  $k_0$  and  $S_{ap}$ . The constant,  $k_0$ , is larger when the catalyst material is more active, while  $S_{ap}$  is larger with a more closely spaced catalyst. The latter, however, not only produces a larger pressure drop but makes the catalyst more susceptible to dust plugging (Figure 3-2). Therefore, usually a granular catalyst with a 3-6 mm diameter is used for clean gas while a honeycomb configuration with a 5-8 mm channel diameter and a parallel plate with a 4-7 mm clearance are used for dusty gas.

The inlet  $NH_3/NO_x$  mole ratio also influences the  $NO_x$  removal efficiency as shown in Figure 3-3. A larger mole ratio produces a higher efficiency and a larger amount of unreacted ammonia leaving the reactor. In practice, a mole ratio between 0.83 and 1.0 is generally used to attain 80-90%  $NO_x$  removal and maintain  $NH_3$  emissions below 5 ppm.

For a catalyst with a given SV,  $NH_3/NO_x$  mole ratio and temperature, the  $NO_x$  removal efficiency as well as ammonia reaction ratio changes little with the inlet  $NO_x$  concentration. This indicates that both outlet  $NO_x$  and  $NH_3$  concentrations increase with inlet  $NO_x$  concentration. Therefore, in order to maintain both  $NO_x$  removal efficiency and unreacted  $NH_3$  at a constant level, a large amount of catalyst (smaller SV) is needed with an increase in inlet  $NO_x$  (Figure 3-4). The relationship between  $NO_x$  removal efficiency and catalyst requirements at a constant inlet  $NO_x$  concentration and unreacted  $NH_3$  level is shown in Figure 3-5.



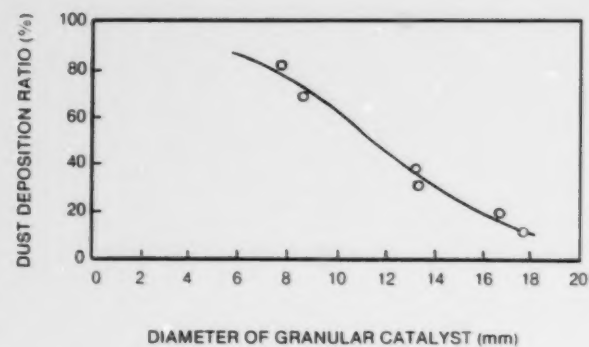
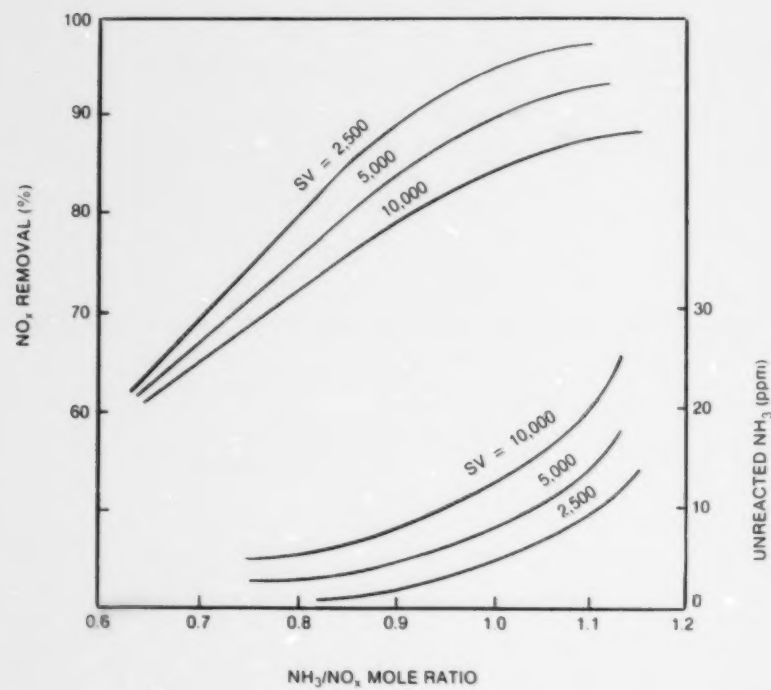


Figure 3-2 Catalyst Size vs. Dust Deposition for Oil-Fired Dust. (Hitachi Ltd.)



(Honeycomb Catalyst; low-sulfur oil, inlet  $\text{NO}_x$ : 150 ppm)

Figure 3-3 SCR for Oil-Fired Boiler Flue Gas at 350°C.

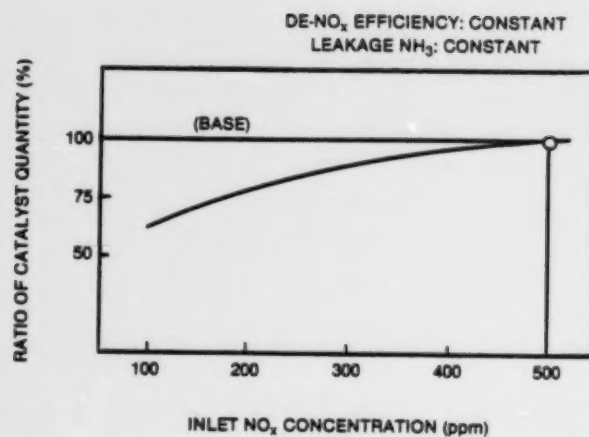


Figure 3-4 NO<sub>x</sub> Concentration vs. Catalyst Quantity. (2)

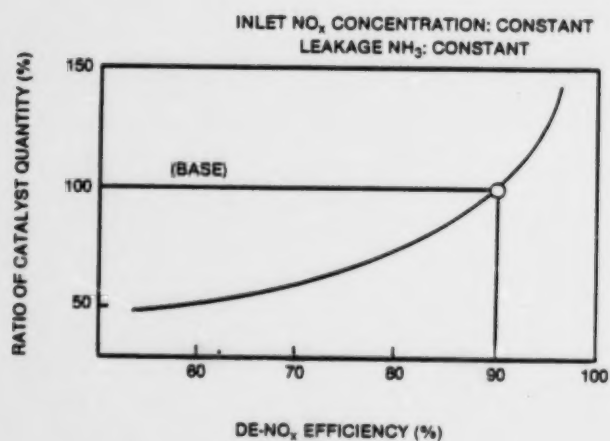


Figure 3-5 De-NO<sub>x</sub> Efficiency vs. Catalyst Quantity. (2)

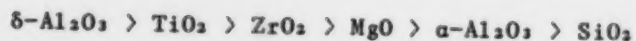


### 3.2 COMPOSITION AND PROPERTIES OF SCR CATALYSTS

#### 3.2.1 History

SCR catalysts have been produced by many manufacturers. The four major manufacturers are Catalyst and Chemicals, Inc., NGK Insulators Co., Sakai Chemical, and Nihon Shokubai Kagaku which produce various types of ceramic catalysts with honeycomb, ring, tube, and pellet configurations. SCR process developers such as MHI, IHI, KHI, JGC Corp., and Kurabo have conducted their own studies on SCR catalysts and have provided manufacturers with specifications for use in catalyst production. Other process developers produce catalysts themselves; Hitachi Ltd. and Hitachi Zosen make metal-based catalysts while Sumitomo Chemical and Kobe Steel manufacture ceramic ones.

At an early stage in SCR development, catalysts based on alumina carriers were used predominantly. At that time,  $\delta$ - $\text{Al}_2\text{O}_3$  was popular as a heat resistant carrier due to its large surface area and high catalytic activity. The relationships between the surface areas of various carriers are shown below (1):



Catalysts based on ferric oxide also have been used. Ferric oxide is catalytically active and can be obtained both as a natural mineral and as a by-product.

A problem associated with both alumina- and ferric oxide-based catalysts is that they have been found to be poisoned by  $\text{SO}_x$  in the flue gas. This occurs because of the formation of sulfate which tends to plug the small pores of the catalyst and reduce its surface area and activity. Although the sulfate can be decomposed by heating it to 700-800°C, the treatment requires a substantial amount of energy.

More recently, titania ( $\text{TiO}_2$ )-based catalysts have become popular for dirty gas treatment because of their high activity and resistance to  $\text{SO}_x$ . The relative  $\text{SO}_x$  resistances of the catalyst carriers are shown below (1):



The properties of various catalyst carriers are compared in Table 3-1.

TABLE 3-1. COMPARISON OF CATALYST'S CARRIER CHARACTERISTICS (KAWASAKI HEAVY INDUSTRIES)

| Characteristics                      | Material |               |           |      |         |
|--------------------------------------|----------|---------------|-----------|------|---------|
|                                      | Alumina  | Ferric Oxides | Silicates | Tuff | Titania |
| $\text{SO}_x$ resistivity            | C        | D             | A         | B    | A       |
| Initial activity for $\text{DeNO}_x$ | A        | C             | C         | B    | A       |
| Physical strength                    | B        | D             | A         | A    | C       |
| Durability                           | C        | D             | C         | B    | A       |
| Cost of catalyst                     | C        | B             | C         | A    | D       |

Note: Symbols A - D indicate ratings with A being the best.

Adding  $\text{V}_2\text{O}_5$  to  $\text{TiO}_2$  produces a highly active SCR catalyst. However, a drawback is that vanadium promotes the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  which causes ammonium bisulfate deposits in the air preheater. Recent efforts to improve SCR catalysts have concentrated on development of an active catalyst which is not poisoned by  $\text{SO}_x$  and has little  $\text{SO}_2$  oxidation capability.

Low-temperature catalysts active at 150-250°C also have been evaluated for use with low-temperature gases such as those from coke ovens and sintering machines. The greatest problem with the low-temperature catalyst is that ammonium bisulfate deposits on it. In practice, the deposits are removed

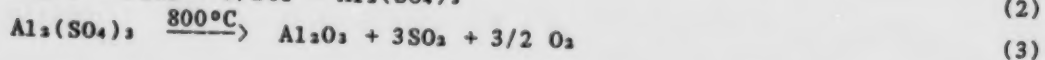
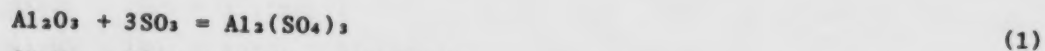
by periodically heating the catalyst above 400°C. This heating process is necessary to restore catalytic activity.

Ammonia decomposition catalysts were studied and used a few years ago but have not been developed. This type of catalyst tends to be poisoned by SO<sub>x</sub> and to oxidize a considerable portion of SO<sub>2</sub> to SO<sub>3</sub>. In recent practice, unreacted NH<sub>3</sub> has been reduced by using a low NH<sub>3</sub>/NO<sub>x</sub> mole ratio and an increased amount of SCR catalyst.

### 3.2.2 Alumina-Based Catalysts

Most alumina carrier catalysts are in the form of δ-Al<sub>2</sub>O<sub>3</sub> which has a large surface area and high activity. This type of catalyst has been used with clean gas containing little or no SO<sub>x</sub>. The performance of alumina-based catalysts for clean gases is shown in Figure 3-6. A catalyst made of alumina impregnated with Cr<sub>2</sub>O<sub>3</sub> shows a high activity around 250°C, while one with Fe<sub>2</sub>O<sub>3</sub> shows a high activity around 430°C. A catalyst active at 300-400°C can be obtained by using both Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> or V<sub>2</sub>O<sub>5</sub> and Cr<sub>2</sub>O<sub>3</sub>.

The alumina in δ form readily reacts with SO<sub>2</sub> to form Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> with reduced surface area and activity (see Figure 3-7). Even though a gas may contain SO<sub>2</sub> and no SO<sub>3</sub>, a portion of SO<sub>2</sub> is oxidized to SO<sub>3</sub> on the catalyst surface and reacts with Al<sub>2</sub>O<sub>3</sub>. When the poisoned carrier is heated to 800°C, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> decomposes to regenerate Al<sub>2</sub>O<sub>3</sub> and catalytic activity is restored. These reactions are:



However, the heating requires a considerable amount of energy and is not economical. Heating δ-Al<sub>2</sub>O<sub>3</sub> to 1100°C, produces α-Al<sub>2</sub>O<sub>3</sub> which is resistant to SO<sub>x</sub>. However, α-Al<sub>2</sub>O<sub>3</sub> has a much smaller surface area and is less active than δ-Al<sub>2</sub>O<sub>3</sub>. Since SO<sub>x</sub>-resistant catalysts based on TiO<sub>2</sub> have become popular, alumina-based catalysts now are seldom used for gas containing SO<sub>x</sub>.

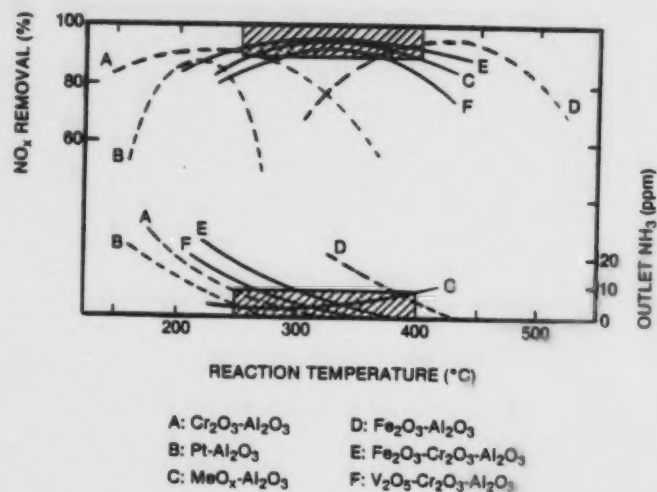


Figure 3-8 Criteria for Catalysts Used with Clean Gas. (1)

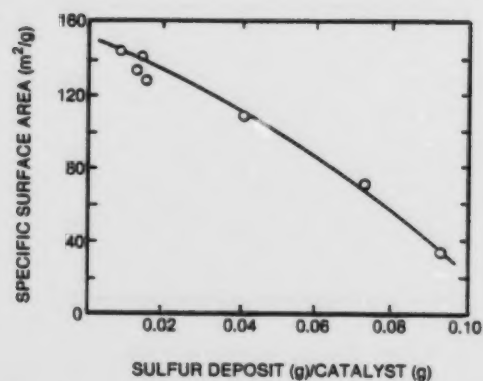


Figure 3-7 Deactivation of Catalyst on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Carrier by SO<sub>x</sub>. (1)

### 3.2.3 Fe<sub>2</sub>O<sub>3</sub>-Based Catalysts

Fe<sub>2</sub>O<sub>3</sub>-based ring-shaped catalysts were used several years ago at a few SCR plants but they were found to be poisoned by SO<sub>x</sub>. Nippon Kokan recently began using a special type of iron ore as the SCR catalyst to treat flue gas from an iron sintering machine. Contaminated by SO<sub>x</sub> and dust, the catalyst, along with other iron ores, is used for steel production. Catalyst and Chemicals, Inc. recently studied the production of a low-cost Fe<sub>2</sub>O<sub>3</sub> catalyst using red mud, a useless by-product of aluminum production, and limonite, a neutral mineral mined in the Aso and Kurohime Mountains (3).

The chemical composition of the red mud and limonite catalyst is shown in Table 3-2. The red mud's major component is highly crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; limonite is composed of  $\alpha$ -FeOOH and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with low crystallinity.

TABLE 3-2. CHEMICAL COMPOSITION OF RED MUD AND LIMONITE CATALYSTS (3)  
(%, on dry basis)

|                                | Red Mud  | Limonite |
|--------------------------------|----------|----------|
| Fe <sub>2</sub> O <sub>3</sub> | 52-55    | 84-85    |
| Al <sub>2</sub> O <sub>3</sub> | 20-27    | 13       |
| SiO <sub>2</sub>               | 7-10     | 13-14    |
| TiO <sub>2</sub>               | 7-10     | Trace    |
| CaO                            | 0-2.5    | 0.1      |
| MgO                            | -        | 0.15     |
| Na <sub>2</sub> O              | 3-5      | 0.3      |
| K <sub>2</sub> O               | Trace    | 0.3      |
| SO <sub>4</sub>                | 0.3      | 0.3      |
| MnO                            | Trace    | 0.4      |
| (H <sub>2</sub> O)             | About 80 | 30-40    |

During the first stage of catalyst production, the red mud is washed with sulfuric acid and water to remove sodium. The red mud and limonite then are combined with water, kneaded, shaped and calcined to produce pellets 3 mm in diameter. The catalyst pellets (25 ml) are placed in a reactor tube. Then a synthetic gas containing 500 ppm NO, 500 ppm SO<sub>2</sub>, 3% O<sub>2</sub>, 10 - 15% H<sub>2</sub>O, with



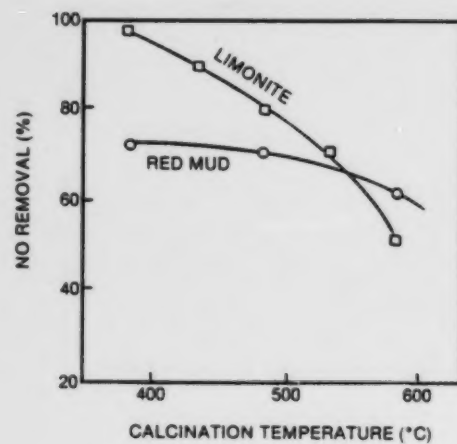
600 or 750 ppm  $\text{NH}_3$  is passed through the catalyst bed at 200–380°C with an SV of 10,000 or 6,000  $\text{hr}^{-1}$ .

Figure 3-8 shows the effect of the catalyst's calcination temperature on its initial activity (before  $\text{SO}_x$  poisoning). The limonite was highly active when calcined at 400°C and became much less so when calcination took place at higher temperatures. Since SCR usually takes place at 300–400°C, calcination of the catalyst at 400–500°C may be adequate to produce good activity and sufficient physical strength. The red mud catalyst was not very active when calcined at 400°C.

The effects of adding various compounds to the catalysts are shown in Figure 3-9. Red mud's activity was increased by the addition of  $\text{V}_2\text{O}_5$  and  $\text{CuO}$  but decreased when  $\text{SnO}_2$  was added. The optimum amount of  $\text{V}_2\text{O}_5$  was 5–10% of the amount of the red mud.  $\text{TiO}_2$  increased the activity of limonite.

Figure 3-10 shows the increase in  $\text{SO}_4$  and decrease in  $\text{NO}_x$  removal efficiency which resulted when three types of catalysts were exposed to flue gas from an oil-fired boiler. After varying exposure periods up to 1,200 hours, the catalysts were subjected to both an  $\text{SO}_4$  analysis and an  $\text{NO}_x$  removal test. Limonite with  $\text{TiO}_2$  calcined at 500°C showed a high initial efficiency which decreased rapidly during exposure (with the concurrent increase in  $\text{SO}_4$ ). Virtually all of the  $\text{Fe}_2\text{O}_3$  was converted to  $\text{Fe}_2(\text{SO}_4)_3$  after 200 hours exposure. Limonite calcined at 700°C with  $\text{TiO}_2$  was inactive although it became more active with an exposure of 200 to 600 hours. Red mud calcined at 500°C was moderately active and remained that way during a period of 1,200 hours.

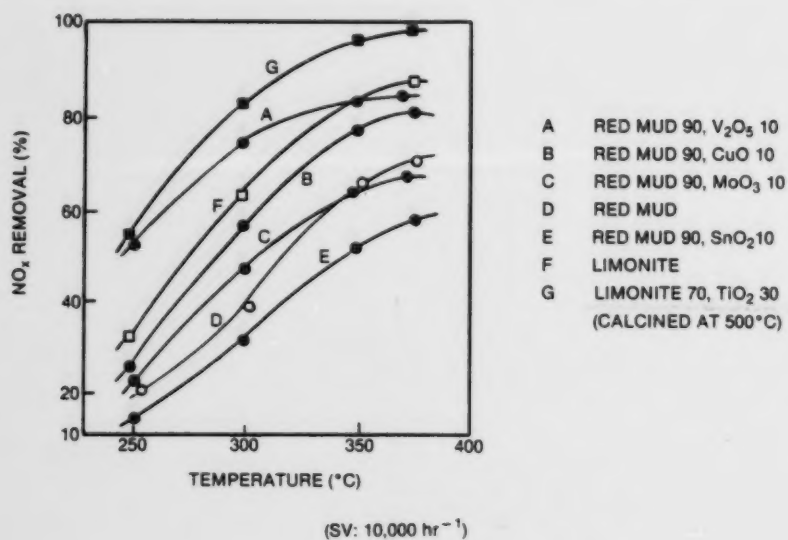
Figure 3-11 shows the results of the exposure tests on red mud catalysts which contained additives of  $\text{TiO}_2$  or  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$ . The improved red mud catalysts maintained fairly good activity even after 3,000 hours of exposure. This indicates that it may be possible to produce a relatively inexpensive  $\text{SO}_x$ -resistant catalyst using red mud.



(350°C; SV: 6,000 hr<sup>-1</sup>; NO: 500 ppm; NH<sub>3</sub>: 700 ppm)

Figure 3-8 Calcination Temperature vs. Initial Activity. (3)

70A2699



- A RED MUD 90, V<sub>2</sub>O<sub>5</sub> 10
- B RED MUD 90, CuO 10
- C RED MUD 90, MoO<sub>3</sub> 10
- D RED MUD
- E RED MUD 90, SnO<sub>2</sub> 10
- F LIMONITE
- G LIMONITE 70, TiO<sub>2</sub> 30 (CALCINED AT 500°C)

Figure 3-9 Effect of Additives on NO<sub>x</sub> Removal.

70A2700



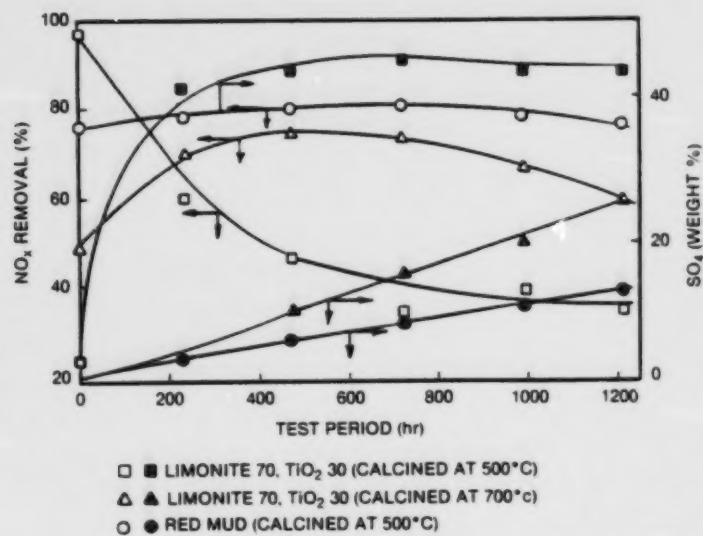


Figure 3-10 Catalyst Tests with Oil-Fired Boiler Flue Gas. (3)

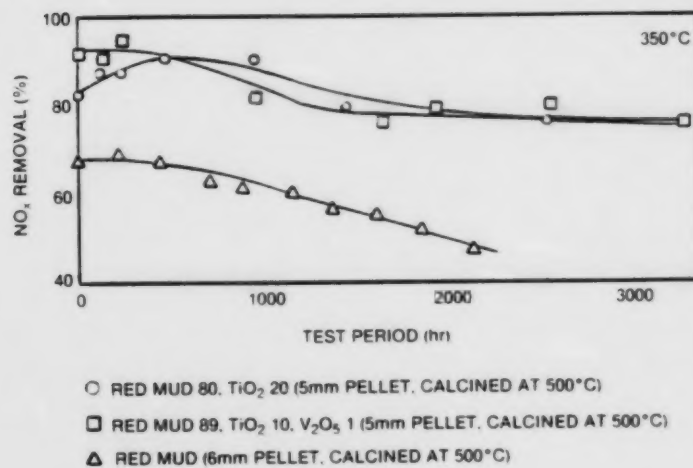


Figure 3-11 Additional Catalyst Tests with Oil-Fired Boiler Flue Gas. (3)

### 3.2.4 TiO<sub>2</sub>-Based Catalysts

Titania (TiO<sub>2</sub>), in the form of anathase, is catalytically active and has a good resistance to SO<sub>x</sub>. Its activity can be increased by adding base metal oxides. As shown in Figures 3-12 and 3-13, Vanadium (V) is a most effective additive for this purpose. For this reason, a TiO<sub>2</sub>-based catalyst containing 1-5% V<sub>2</sub>O<sub>5</sub> has been most popular for gas containing SO<sub>x</sub>. However, a common problem associated with this catalyst is the oxidation of a portion of the SO<sub>2</sub> to SO<sub>3</sub>. During cooling, the SO<sub>3</sub> combines with NH<sub>3</sub> and H<sub>2</sub>O to form NH<sub>4</sub>HSO<sub>4</sub> which results in the plugging of the air preheater elements. The oxidation ratio is larger with a lower SV and a smaller NH<sub>3</sub>/NO<sub>x</sub> mole ratio; NH<sub>3</sub> works as a reducing agent to lower the oxidation ratio (Figure 3-14).

When Cu, Co, and Ce are used as additives to the TiO<sub>2</sub>-based catalyst, a substantial amount of oxidation occurs; when V is used with Mo and W only a slight amount of oxidation occurs.

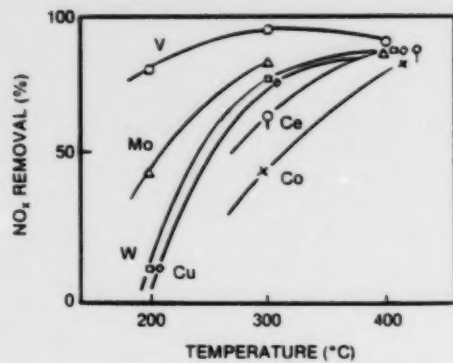
Catalyst producers are making efforts to lower the oxidation ratio. A common method is to replace a considerable portion of V with other metals such as Mo or W (Figure 3-15). With the replacement, the NO<sub>x</sub> removal efficiency is slightly lowered while the oxidation ratio is lowered to a much greater extent. Table 3-3 shows the TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> catalyst (108-H) and improved catalysts (109 H - 111 HC).

The TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> catalyst is poisoned by alkali compounds, particularly by potassium at low temperatures (Figure 3-16). Figure 3-17 shows that a catalyst using two kinds of selected base metals is poisoned to a lesser degree.

## 3.3 LOW-TEMPERATURE CATALYSTS

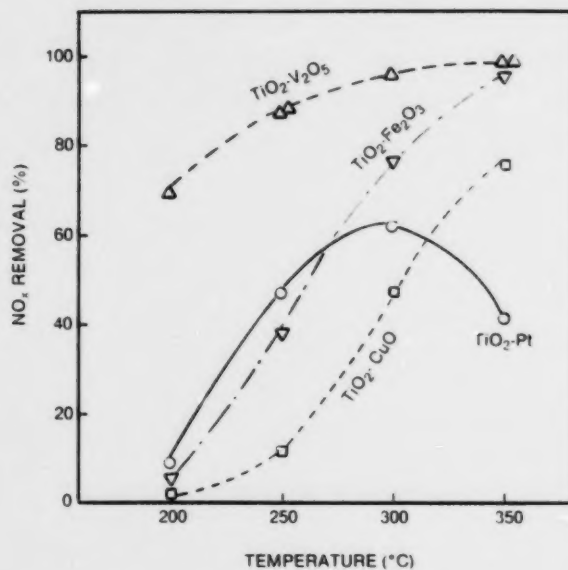
### 3.3.1 Introduction

For some gas sources, such as coke ovens and iron-ore sintering machines, the temperature of the gas stream requiring NO<sub>x</sub> removal is low (150-250°C). Since heating the gas to 300-400°C requires a large amount of energy, low-



(metal oxide:  $\text{TiO}_2 = 5:100$ , 3.3mm pellet;  
 $\text{NO}$ : 200 ppm;  $\text{NH}_3$ : 200 ppm;  $\text{SO}_2$ : 500 ppm;  
 $\text{O}_2$ : 1.5%;  $\text{H}_2\text{O}$ : 10%;  $\text{SV} = 10,000 \text{ hr}^{-1}$ )

Figure 3-12 Additives' Effect on  $\text{TiO}$ -Based Catalyst. (4)



(3mm pellets;  $\text{SV} = 15,000 \text{ hr}^{-1}$ ;  $\text{NO}$ : 150 ppm;  
 $\text{NH}_3$ : 180 ppm;  $\text{O}_2$ : 4%;  $\text{H}_2\text{O}$ : 10%;  $\text{SO}_2$ : 1,000 ppm)

Figure 3-13 Activity of  $\text{TiO}$ -Based Catalyst. (5)

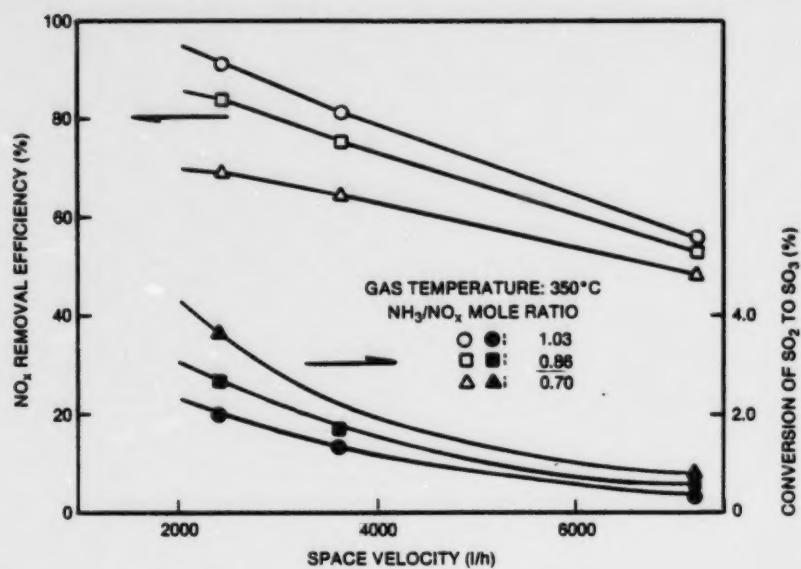


Figure 3-14 NO<sub>x</sub> Removal and SO<sub>2</sub> Oxidation. (8)

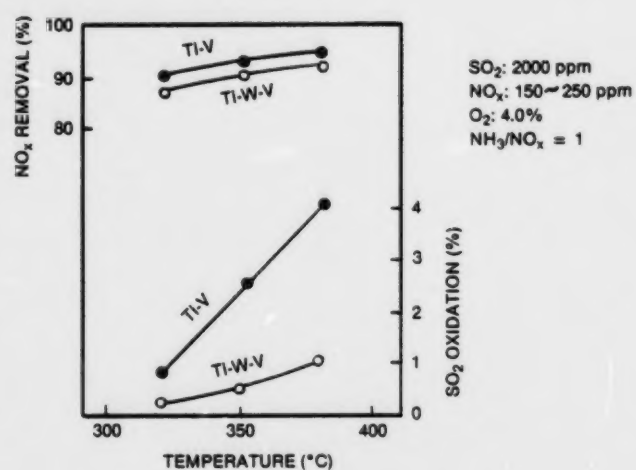


Figure 3-15 Performance of Ti-V and Ti-W-V Catalysts.  
(Kawasaki Heavy Industries)

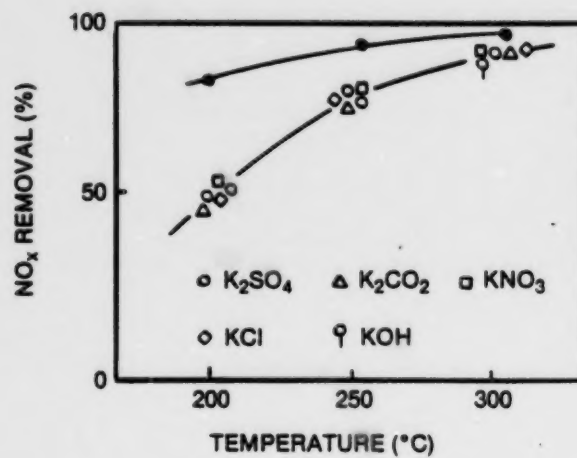


Figure 3-16 Effect of Potassium on  $\text{TiO}_2\text{-V}_2\text{O}_5$  Catalyst. (4)

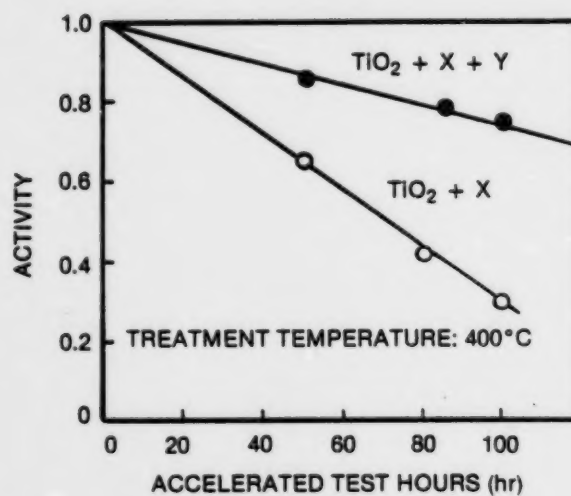


Figure 3-17 Test Results of Accelerated Deterioration Test with Alkalimetal Sulfate. (7)

TABLE 3-3. PERFORMANCE OF HONEYCOMB CATALYSTS (NIHON SHOKUBAI KAGAKU)  
(Gas Composition: NO<sub>x</sub> 180-200 ppm, SO<sub>x</sub> 150-200 ppm), CO<sub>2</sub> 7-10%, H<sub>2</sub>O 7-10%, O<sub>2</sub> 7-10%, NH<sub>3</sub>/NO<sub>x</sub> mole ratio: 1.0, Area Velocity 1.0 m/hr)

| Catalyst No.        | SV <sub>-1</sub><br>(hr <sup>-1</sup> ) | NO <sub>x</sub> Removal (%) at |       |       | SO <sub>2</sub> oxidation (%) at |       |
|---------------------|-----------------------------------------|--------------------------------|-------|-------|----------------------------------|-------|
|                     |                                         | 300°C                          | 350°C | 380°C | 350°C                            | 380°C |
| 108 H <sup>a</sup>  | 4,830                                   | 92                             | 96    | 97    | 2.1                              | 4.0   |
| 109 H <sup>a</sup>  | 4,830                                   | 87                             | 94    | 95    | 0.5                              | 1.0   |
| 110 H <sup>a</sup>  | 4,830                                   | 77                             | 85    | 89    | 0.05                             | 0.1   |
| 111 H <sup>a</sup>  | 4,830                                   | 84                             | 92    | 94    | 0.2                              | 0.4   |
| 109 HC <sup>b</sup> | 3,710                                   | 79                             | 87    | 90    | 0.5                              | 1.1   |
| 111 HC <sup>b</sup> | 3,710                                   | 76                             | 84    | 88    | 0.2                              | 0.4   |

<sup>a</sup>Honeycomb for oil-fired flue gas: channel diameter 6 mm, wall thickness 1.4 mm.

<sup>b</sup>Honeycomb for coal-fired flue gas: channel diameter 3 mm, wall thickness 1.8 mm.



temperature catalysts active at 150–250°C, have been developed. However, the following problems have occurred with this type of catalyst: (1) the reaction rate is generally slow; (2) ammonium bisulfate deposits on the catalyst below 300°C; and (3) poisoning by potassium compounds occurs more seriously at lower temperatures (Figure 3-16).

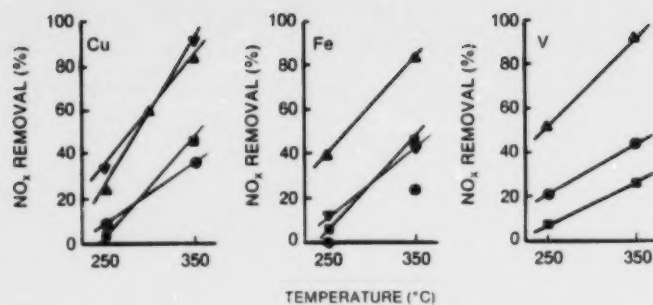
Kureha Chemical has developed a catalyst which is active at 150°C (8). However, this catalyst, is seriously poisoned by  $\text{SO}_x$  in the gas stream and therefore has not been used commercially.  $\text{SO}_x$ -resistant catalysts active at 200–250°C also have been developed by several manufacturers. Even with an  $\text{SO}_x$ -resistant catalyst, ammonium bisulfate deposits form, thereby lowering catalytic activity. To increase its activity, the catalyst occasionally must be heated above 400°C. This heating can be achieved either by mixing a hot gas with the low-temperature gas or by removing the catalyst from the reactor (moving bed) for thermal treatment.

Many of the early low-temperature catalysts were based on zeolite combined with various metals, as shown in Figures 3-18 (5) and 3-19 (11). They generally consumed less than 1 mol  $\text{NH}_3$  to 1 mol  $\text{NO}$ , but were no more efficient than the  $\text{TiO}_2$ - $\text{V}_2\text{O}_5$  catalyst, except for those containing Pt and Pd (which are readily poisoned by  $\text{SO}_x$ ). Most of the recently developed low-temperature catalysts are based on  $\text{TiO}_2$ , except for those developed by Kobe Steel which are alumina-based. (Section 5.6).

### 3.3.2 Catalytic Activity Decrease Caused by Ammonium Bisulfate Deposit

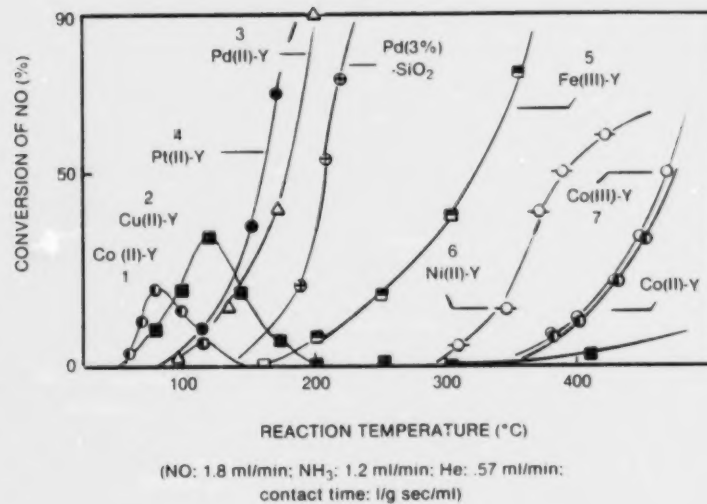
Figure 3-20 illustrates the decreased catalytic activity of  $\text{TiO}_2$ -based metal catalysts during a 100 hour period at 250°C. The decrease is due to ammonium bisulfate deposition. The gas used for the test contained 1,000 ppm  $\text{SO}_2$  without  $\text{SO}_3$ . It is obvious that a portion of  $\text{SO}_2$  is oxidized on the catalyst surface to form the bisulfate. The decrease in catalytic activity was substantial with the Ce catalyst, slightly less severe with the Cu, V, and Co catalysts, and only slight with the Mo and W. Although the catalysts with Mo and W additives were barely affected by the bisulfate, the initial activity of these catalysts was much lower than that of the vanadium catalyst.





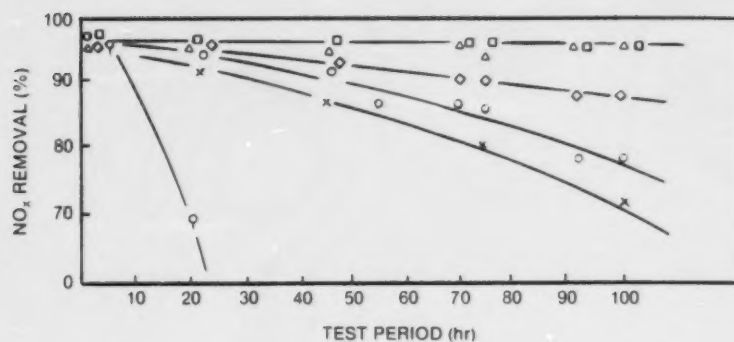
(carrier: • 13X, ■ 5A, ▼ Na-Y, ✕  $\text{NH}_4$ -mordenite  
3mm pellet, SV 15,000  $\text{hr}^{-1}$ )

Figure 3-18 Low-Temperature Catalyst with Zeolite Carrier. (5)



NOTE: The degree of ion exchange is as follows: 1) Co(II)-Y: 70%;  
2) Cu(II)-Y: 68%; 3) Pd(II)-Y: 48%; 4) Pt(II)-Y: 52%;  
5) Fe(III)-Y: 75%; 6) Ni(II)-Y: 80%; 7) Co(III)-Y: 95%.

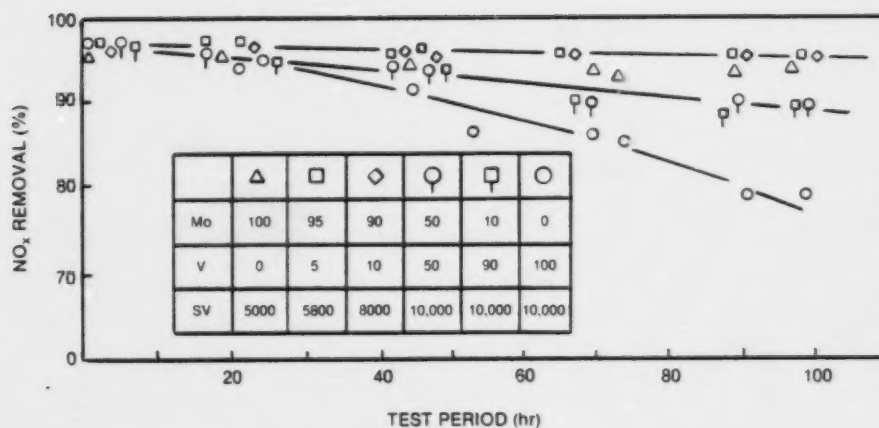
Figure 3-19 Catalytic Activity of Various Transition Metal Ion-Exchanged Y-Type Zeolites for the  $\text{NO-NH}_3$  Reaction.



○ V, SV = 10,000, △ Mo, SV = 5000, □ W, SV = 1700  
 ◇ Cu, SV = 1700, ◊ Ce, SV = 1500, X Co, SV = 1000

(NO: 200 ppm; NH<sub>3</sub>: 300 ppm; SO<sub>2</sub>: 1000 ppm;  
 O<sub>2</sub>: 1.5%; H<sub>2</sub>O: 10%; 3mm pellet)

Figure 3-20 Decrease in Catalytic Activity of TiO<sub>2</sub>-Metal Oxide Catalysts at 250°C. (4)



(NO: 200 ppm; NH<sub>3</sub>: 300 ppm; SO<sub>2</sub>: 1000 ppm; O<sub>2</sub>: 1.5%; H<sub>2</sub>O: 10%; 3mm pellet)

Figure 3-21 Decrease in Activity of TiO<sub>2</sub>-MoO-V<sub>2</sub>O<sub>5</sub> Catalyst at 250°C. (4)

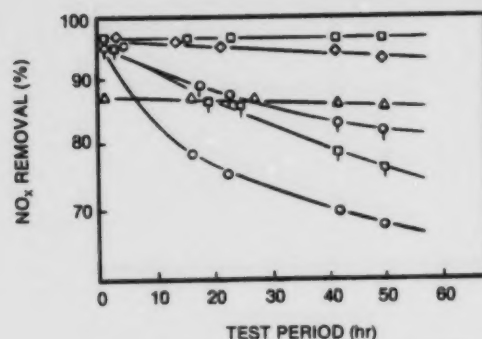
Figures 3-21 and 3-22 show the results of tests performed on the  $\text{TiO}_2\text{-MoO}_3\text{-V}_2\text{O}_5$  catalysts at 250° and 200°C, respectively. A more noticeable decrease in catalytic activity occurred at 200°C than at 250°C. A catalyst with an Mo:V ratio of 95:5 exhibited only a slight decrease in activity during a 50 hour test period at 200°C, as well as during 100 hours at 250°C.

Figure 3-23 shows the decrease in catalytic activity which occurs when the catalyst is used with a gas containing 200 ppm  $\text{SO}_2$  and 50 ppm  $\text{SO}_3$ . This decrease was considerably smaller than that with gas containing 1000 ppm  $\text{SO}_2$  without  $\text{SO}_3$ , as shown in Figure 3-21. These results indicate that a considerable portion of  $\text{SO}_3$  is converted to  $\text{SO}_2$  on the catalyst surface.

Table 3-4 shows the properties and chemical composition of  $\text{TiO}_2\text{-V}_2\text{O}_5\text{-MoO}_3$  catalysts before and after use at 250°C for 100 hours and 200°C for 50 hours. With use,  $\text{NH}_4$  and  $\text{SO}_4$  deposited on the catalysts, lowering the surface area and decreasing the pore volume. Both the deposition and the lowered activity occurred to a greater degree with the catalyst that contained more vanadium. The  $\text{NH}_4/\text{SO}_4$  weight ratio ranged from 0.12 to 0.25 and the  $\text{NH}_4/\text{SO}_4$  mole ratio from 0.6 to 1.33, indicating that the deposits were mostly ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ).

### 3.3.3 Use of Heating to Recover Catalytic Activity

The activity of  $\text{TiO}_2$ -based catalysts can be restored by heating them to 400-450°C. In one series of tests, a catalyst contaminated with ammonium bisulfate was heated for three hours at 400°, 430°, 450° and 470°C and then again used for SCR at 200°, 250° and 300°C (Figure 3-24). The activity of the catalyst heated at 450° and 470°C was almost equal to that of the fresh catalyst. Figure 3-25 shows that by heating the catalyst at 450°C for three hours, virtually all of the  $\text{NH}_4$  and  $\text{SO}_4$  were removed and the catalytic activity was restored. Table 3-5 shows that when the used catalyst is heated at 450°C for three hours, both surface area and pore volume increased to approach those of the fresh catalyst.

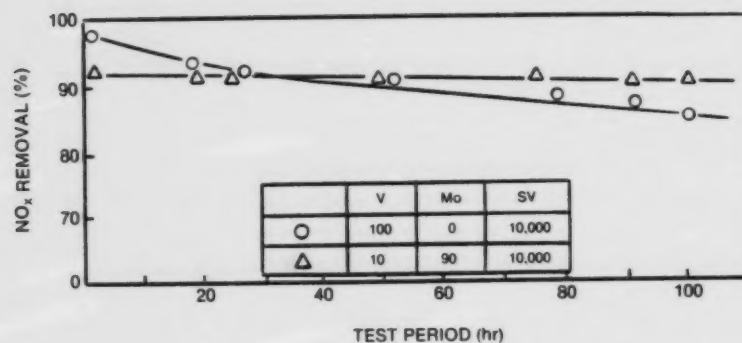


|    | △    | □    | ◇    | ○    | ◻    | ○    |
|----|------|------|------|------|------|------|
| Mo | 100  | 95   | 90   | 50   | 10   | 0    |
| V  | 0    | 5    | 10   | 50   | 90   | 100  |
| SV | 3000 | 3000 | 4000 | 6000 | 6000 | 6000 |

(NO: 200 ppm; NH<sub>3</sub>: 300 ppm; SO<sub>2</sub>: 1000 ppm;  
O<sub>2</sub>: 1.5%; H<sub>2</sub>O: 10%; 3mm pellet)

Figure 3-22 Decrease in Activity of TiO<sub>2</sub>-MoO-V<sub>2</sub>O<sub>5</sub> Catalyst at 200°C. (4)

70A2713



(NO<sub>x</sub>: 200 ppm; NH<sub>3</sub>: 300 ppm; SO<sub>2</sub>: 200 ppm; SO<sub>3</sub>: 50 ppm;  
O<sub>2</sub>: 1.5%; H<sub>2</sub>O: 10%; 3mm pellet)

Figure 3-23 Decrease in Activity of TiO<sub>2</sub>-MoO-V<sub>2</sub>O<sub>5</sub> Catalyst at 250°C. (Gas contains SO<sub>3</sub>) (4)

70A2714

TABLE 3-4. PROPERTIES AND COMPOSITIONS OF CATALYSTS (FRESH AND USED)

| Ratio<br>V:Mo | Reaction<br>Temp.<br>(°C) | Surface<br>Area<br>(m <sup>2</sup> /g) | Pore<br>Volume<br>(ml/g) | Chemical Composition |                     |                                  |
|---------------|---------------------------|----------------------------------------|--------------------------|----------------------|---------------------|----------------------------------|
|               |                           |                                        |                          | NH <sub>4</sub> (%)  | SO <sub>4</sub> (%) | NH <sub>4</sub> /SO <sub>4</sub> |
| 100:0         | f <sup>a</sup>            | 31                                     | 0.27                     | -                    | -                   | -                                |
|               | 250 <sup>b</sup>          | 17                                     | 0.18                     | 1.3                  | 10.9                | 0.12                             |
|               | 200 <sup>c</sup>          | 17                                     | 0.19                     | 1.6                  | 10.2                | 0.16                             |
| 0:100         | f                         | 34                                     | 0.25                     | -                    | -                   | -                                |
|               | 250                       | 31                                     | 0.25                     | 0.1                  | 0.5                 | 0.20                             |
|               | 200                       | 32                                     | 0.26                     | 0.2                  | 0.8                 | 0.25                             |
| 90:10         | f                         | 34                                     | 0.28                     | -                    | -                   | -                                |
|               | 250                       | 17                                     | 0.23                     | 1.0                  | 7.1                 | 0.14                             |
|               | 200                       | 16                                     | 0.20                     | 1.6                  | 8.3                 | 0.19                             |
| 50:50         | f                         | 33                                     | 0.29                     | -                    | -                   | -                                |
|               | 250                       | 17                                     | 0.25                     | 0.8                  | 4.7                 | 0.17                             |
|               | 200                       | 20                                     | 0.23                     | 1.3                  | 5.7                 | 0.23                             |
| 10:90         | f                         | 35                                     | 0.30                     | -                    | -                   | -                                |
|               | 250                       | 26                                     | 0.29                     | 0.2                  | 1.2                 | 0.17                             |
|               | 200                       | 28                                     | 0.28                     | 0.3                  | 1.3                 | 0.23                             |
| 5:95          | f                         | 35                                     | 0.30                     | -                    | -                   | -                                |
|               | 250                       | 31                                     | 0.29                     | 0.2                  | 0.9                 | 0.22                             |
|               | 200                       | 29                                     | 0.27                     | 0.2                  | 0.8                 | 0.25                             |

<sup>a</sup>Fresh (before use)<sup>b</sup>After used at 250°C for 100 hours<sup>c</sup>After used at 200°C for 50 hours

TABLE 3-5. PROPERTIES AND COMPOSITIONS OF CATALYSTS (FRESH, USED, AND HEATED AT 450°C FOR THREE HOURS)

| Ratio<br>V:Mo | Type   | Surface<br>Area<br>(m <sup>2</sup> /g) | Pore<br>Volume<br>(ml/g) | Chemical Composition |                     |                                  |
|---------------|--------|----------------------------------------|--------------------------|----------------------|---------------------|----------------------------------|
|               |        |                                        |                          | NH <sub>4</sub> (%)  | SO <sub>4</sub> (%) | NH <sub>4</sub> /SO <sub>4</sub> |
| 90:10         | Fresh  | 34                                     | 0.28                     | -                    | -                   | -                                |
|               | Used   | 20                                     | 0.23                     | 0.9                  | 4.3                 | 0.21                             |
|               | Heated | 27                                     | 0.30                     | -                    | -                   | -                                |
| 50:50         | Fresh  | 33                                     | 0.29                     | -                    | -                   | -                                |
|               | Used   | 20                                     | 0.24                     | 0.7                  | 3.2                 | 0.22                             |
|               | Heated | 30                                     | 0.30                     | -                    | -                   | -                                |



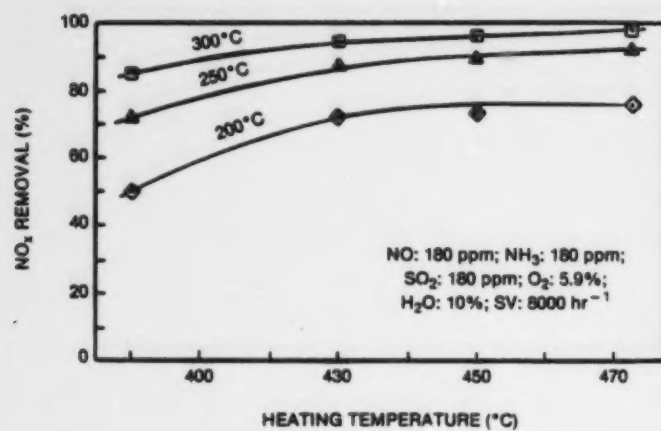


Figure 3-24 Recovery in Activity of Contaminated Catalyst During Three-Hour Heating Period. (9)

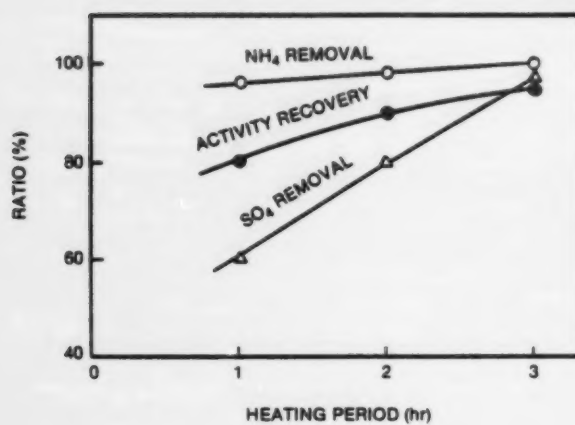


Figure 3-25 Effects of 450°C Thermal Treatment on Catalyst Contaminated with Ammonium Bisulfate. (9)

Figure 3-26 shows that the vanadium-rich catalyst is very active initially, but requires frequent heating because of rapid bisulfate deposition. The  $\text{TiO}_2$ -Mo catalyst has a low initial activity which did not decrease during 100 hours of use; a catalyst with an Mo:V ratio of 90:10 has a fairly high initial activity which decreased slightly with 100 hours of use.

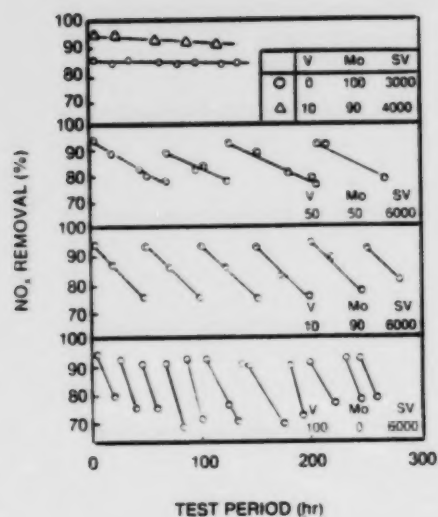
#### 3.3.4 Alkali Poisoning and Poisoning Countermeasures

When alkali is added to the  $\text{TiO}_2$ - $\text{V}_2\text{O}_5$  catalyst, the catalyst becomes less active (Figure 3-27). Potassium proved to be even more poisonous to this catalyst than sodium. Figure 3-28 compares the poisoning of various  $\text{TiO}_2$ -metal oxide catalysts. Mo and W catalysts showed a considerable amount of poisoning. Figure 3-29 shows the poisoning of  $\text{TiO}_2$ -MoO- $\text{V}_2\text{O}_5$  catalysts; poisoning was more extensive with a larger Mo:V ratio.

Tests have indicated that alkali compounds present in the contaminated catalysts can be removed with a hot water wash or with aqueous solutions of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ . Figure 3-30 shows how washing restores catalytic activity. The  $\text{TiO}_2$ - $\text{V}_2\text{O}_5$  catalyst's activity is partially restored by a hot water wash and almost completely restored after a wash with aqueous solutions of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ . During the same test, the activity of the  $\text{TiO}_2$ -MoO catalyst was not restored by the wash. The activity of the  $\text{TiO}_2$ - $\text{V}_2\text{O}_5$ -MoO catalyst (V:Mo=10:90) recovered well after a wash with a mixed solution of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ .

Table 3-6 shows the change in the  $\text{TiO}_2$ - $\text{V}_2\text{O}_5$  catalyst caused by alkali poisoning and the subsequent washing of the poisoned catalyst with hot water and a mixture of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ . After the wash, most of potassium was removed and the pore volume was restored. The  $\text{V}_2\text{O}_5$  decreased during washing because it is slightly soluble in water and the  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  solution. For this reason, it may be necessary to add  $\text{V}_2\text{O}_5$  to the catalyst after it has been washed several times.





(NO<sub>x</sub>: 200 ppm; NH<sub>3</sub>: 300 ppm; SO<sub>2</sub>: 1000 ppm;  
O<sub>2</sub>: 1.5%; H<sub>2</sub>O: 10%; 200°C, 3mm pellet)

Figure 3-26 Effect of Thermal Decomposition at 450°C. (4)

70A2717

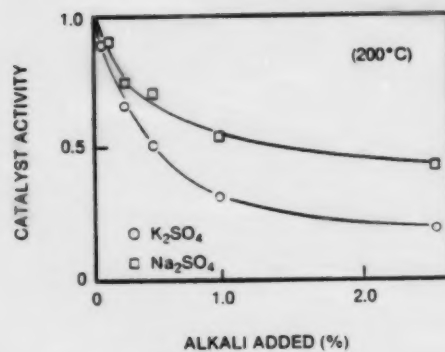


Figure 3-27 Effect of Alkali on TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> Catalyst. (4)

70A2718

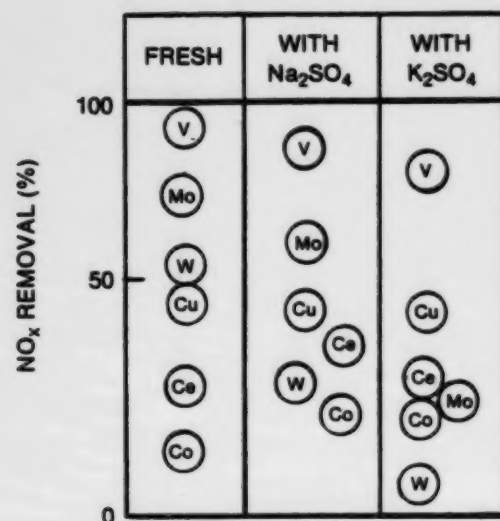


Figure 3-28 Effect of Alkali on  $\text{TiO}_2$ -Metal Oxide Catalysts.

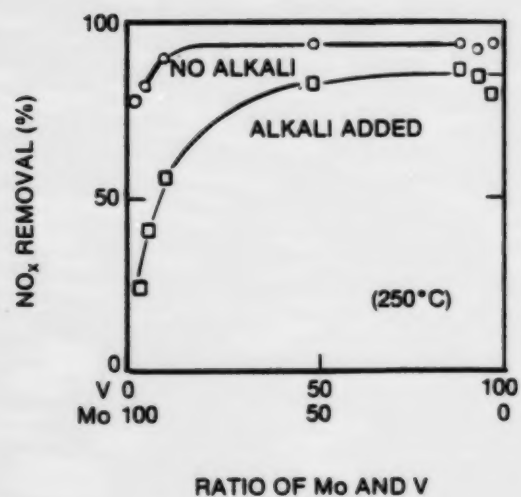


Figure 3-29 Effect of Alkali on  $\text{TiO}_2$ -MoO- $\text{V}_2\text{O}_5$  Catalyst. (4)

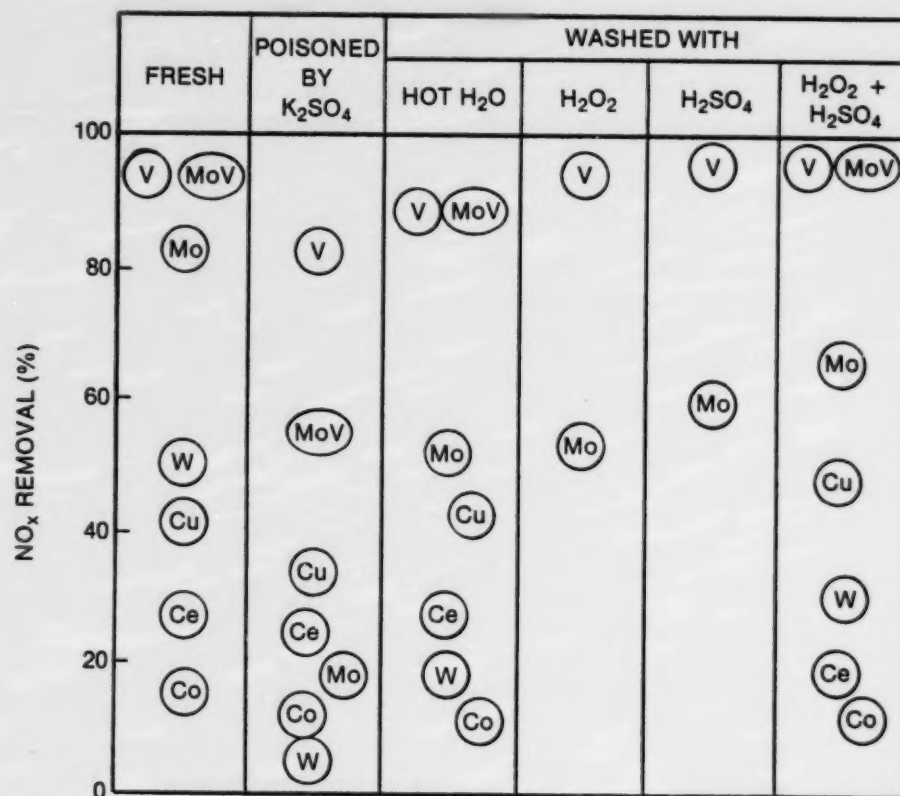


Figure 3-30 K<sub>2</sub>SO<sub>4</sub> Poisoning and Recovery of the TiO<sub>2</sub>-Based Catalyst. (MoV indicates Mo:V = 90:10) (4)

70A2721

TABLE 3-6. CHANGES IN THE  $\text{TiO}_2\text{-V}_2\text{O}_5$  CATALYST CAUSED BY ALKALI ADDITION AND BY WASHING

|                                                                    | Surface<br>Area<br>( $\text{m}^2/\text{g}$ ) | Pore<br>Volume<br>( $\text{ml/g}$ ) | $\text{V}_2\text{O}_5$<br>(%) | $\text{K}_2\text{O}$<br>(%) |
|--------------------------------------------------------------------|----------------------------------------------|-------------------------------------|-------------------------------|-----------------------------|
| (A) Fresh                                                          | 31                                           | 0.27                                | 4.7                           | 0.03                        |
| (B) Alkali added                                                   | 31                                           | 0.25                                | 4.5                           | 0.60                        |
| (C) B was washed by hot water                                      | 31                                           | 0.28                                | 4.1                           | 0.17                        |
| (D) B was washed by $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$ | 30                                           | 0.27                                | 4.0                           | 0.10                        |

### 3.3.5 Summary

The  $\text{TiO}_2\text{-V}_2\text{O}_5$  catalyst is active even at low temperatures of 200–250°C. However, ammonium bisulfate readily deposits on the catalyst at these temperatures and reduces catalytic activity due to the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ . Frequent heating of the catalyst to 450°C is needed to remove the bisulfate and restore activity. A  $\text{TiO}_2\text{-MoO}$  catalyst does not have as much of a problem with ammonium bisulfate deposition but is not very active.  $\text{TiO}_2$ -based catalysts with  $\text{MoO}$  and  $\text{V}_2\text{O}_5$  in a ratio of (90–95):(10–5) may be suitable for low-temperature applications because they are catalytically active and have no problem with bisulfate deposition.

Alkali compounds, particularly those containing potassium, poison the catalysts. This poisoning occurs most seriously at low temperatures. Although the alkali contained in the catalyst can be removed by washing with hot water or aqueous solutions, some  $\text{V}_2\text{O}_5$  is lost in the wash. This means that more  $\text{V}_2\text{O}_5$  must be added and the wash liquor must be treated. For these reasons, it may not be appropriate to treat alkali-rich gas with a low-temperature catalyst.

For boilers, the application of SCR to 300–400°C economizer outlet gas may be preferable to using a low-temperature catalyst for the 150–200°C air-

preheater outlet gas. This is true despite the fact that an existing boiler requires considerable modification for application of SCR to the economizer outlet.

For low-temperature gas such as that from coke ovens (200-250° ), the use of a low-temperature catalyst is preferable to using a conventional catalyst combined with gas heating to 300-350°C. Although the low-temperature catalyst requires occasional heating up to 400°C, it can save a considerable amount of energy compared with continuous gas heating to 300-350°C.

### 3.4 CATALYST SHAPE AND REACTOR TYPE

#### 3.4.1 Introduction

Various types of catalysts and reactors have been in commercial use in Japan, as shown in Table 3-7.

Both spherical- and cylindrical-shaped granular catalysts (3-6 mm diameter) have been used with clean gas. Since only the 0.3mm-thick surface layer of the catalyst is effective for catalytic action, smaller catalysts are more efficient. However, since small catalysts are susceptible to dust plugging, ring or ring-tube catalysts, 10-30 mm in diameter, have been used with gas containing a small amount of dust such as 20 mg/m<sup>3</sup> or less.

A rough calculation indicates that when a gas containing 20 mg/m<sup>3</sup> of dust is sent through a catalyst bed for ten hours at an SV of 5,000 hr<sup>-1</sup>, the volume of the dust in the gas is approximately equal to the volume in the catalyst.



TABLE 3-7. SCR CATALYSTS AND REACTORS SUITABLE FOR VARIOUS GASES

| Gas Type                   | Fuel<br>(Gas Source)                                  | Dust<br>(g/Nm <sup>3</sup> ) | Catalyst Shape                                        | Reactor Type                                               |
|----------------------------|-------------------------------------------------------|------------------------------|-------------------------------------------------------|------------------------------------------------------------|
| Clean                      | Natural gas<br>Kerosene<br>Naphtha                    | Below<br>0.02                | Granule, Ring                                         | Fixed bed                                                  |
| Semi-<br>Dirty             | Heavy oil<br>Coal with<br>hot ESP <sup>b</sup>        | 0.02-0.2                     | Granule, Ring<br>Honeycomb,<br>Plate                  | Moving bed<br>Fixed bed <sup>a</sup>                       |
| Dirty<br>(dusty)           | Coal                                                  | 15-25                        | Granule (in<br>elements)<br>Tube, Plate,<br>Honeycomb | Parallel<br>passage <sup>a</sup><br>Fixed bed <sup>a</sup> |
| Very<br>dirty <sup>c</sup> | Glass furnace,<br>cement kiln<br>sintering<br>machine |                              | Granule                                               | Moving bed                                                 |

<sup>a</sup>Parallel flow type.<sup>b</sup>Electrostatic precipitator.<sup>c</sup>Containing vapor of alkaline compounds which deposit on the catalyst.

Dusty gas can be treated either with a moving bed or a parallel flow reactor. Moving bed reactors have been developed by several vendors. The parallel passage reactor was originally developed by Shell for FGD and later modified by JGC Corp. for SCR. These reactors were first applied commercially several years ago. More recently, parallel flow reactors using parallel flow catalysts with honeycomb, plate and tube configuration have become quite popular. Among the parallel flow catalysts, the honeycomb and plate types have been used most widely.

#### 3.4.2 Moving Bed Reactor

A basic sketch of a moving bed reactor is presented in Figure 3-31. The granular catalyst is charged from the top of the reactor and moves down either intermittently or continuously while the gas is sent through the catalyst

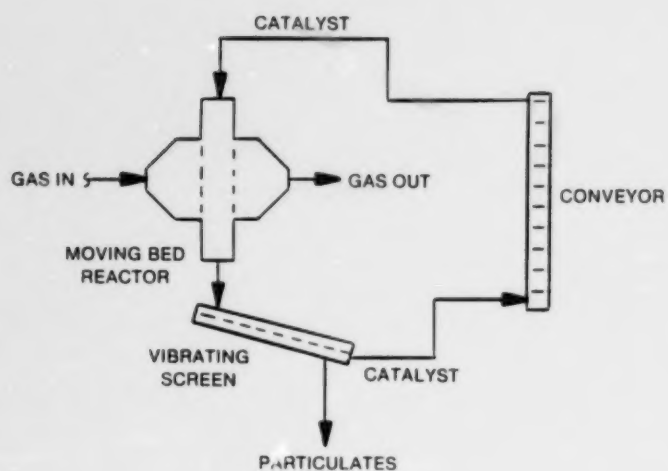


Figure 3-31 Schematic of a Moving Bed Reactor.

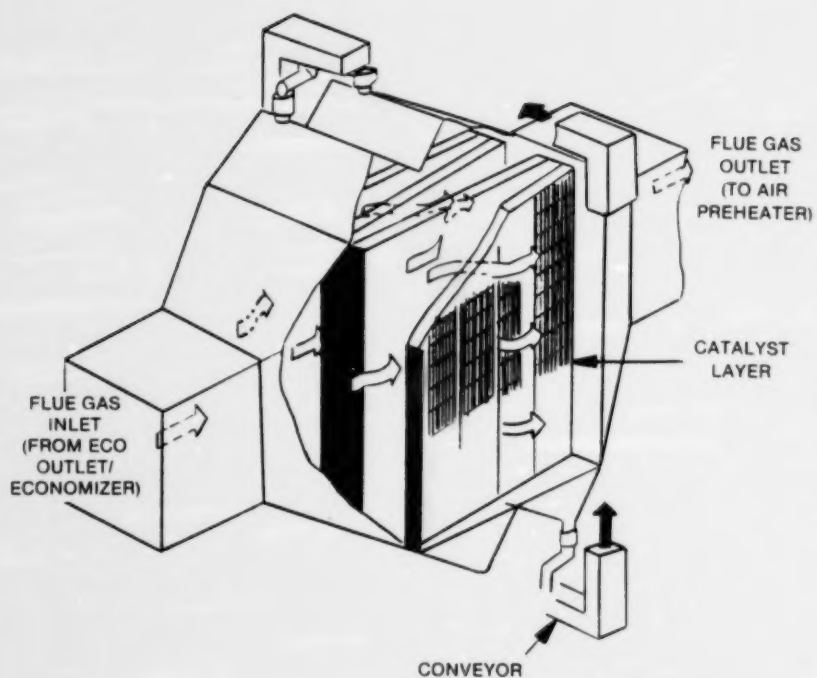


Figure 3-32 Moving Bed Reactor for a Large Amount of Gas. (IHI)



layer in a cross flow (Figure 3-31). The catalyst discharged from the bottom of the reactor is screened to remove dust and returned to the reactor. A larger amount of dust in the gas being heated requires more frequent screening and recycling to keep the pressure drop below a certain level. This results in an increase in power consumption as well as catalyst loss. For practical purposes the dust content of the gas being heated by a moving bed reactor should be no more than 200 mg/Nm<sup>3</sup>.

Moving bed reactors are best suited to dirty gas, such as that from glass melting furnaces, which contains sodium sulfate vapor. The vapor deposits on the catalyst. These reactors are also appropriate for low temperature gas in which ammonium bisulfate deposits on the catalyst. The contaminated catalyst can be withdrawn from the reactor, cleaned by water washing or heating, and returned to the reactor without interrupting plant operation.

Moving bed reactors have a number of advantages over parallel flow reactors:

- (1) The catalyst can be changed without stopping the operation of the system.
- (2) The catalyst is usually granular and is considerably cheaper than parallel flow catalysts. It also can be packed easily in the reactor.
- (3) The moving bed can remove up to about 70% of the dust in the gas and may be well suited to gases for which 70% dust removal is sufficient to meet regulatory requirements. These gases include those from coke ovens and relatively small oil-fired boilers not equipped with dust removal facilities.
- (4) Moving bed reactors may be suitable for low temperature gas or dirty gas which causes deposition on the catalyst.

On the other hand, moving bed reactors have the following disadvantages:

- (1) The operation of a moving bed reactor is more costly and troublesome than that of a fixed bed reactor. The latter has no moving parts and usually does not require an operator.
- (2) A low gas velocity (0.5–1.5 m/sec) is used to maintain a small pressure drop in the reactor. Therefore, when a large amount of gas is being treated, a special reactor design is needed to obtain a large gas flow area and to maintain uniform gas flow and movement of the catalyst (Figure 3-32).
- (3) The reactor cannot easily treat gases containing more than 200 mg/Nm<sup>3</sup> of particulates.
- (4) Attrition of the catalyst tends to occur.

Moving bed reactors have been used in many pilot plants and commercially as well. They also have been used at prototype plants to treat dirty gas from glass melting furnaces and low temperature gas from coke ovens (Table 3-8). For oil- and coal-fired boilers, parallel flow reactors have become more popular since they now have a longer life cycle.

#### 3.4.3 Parallel Flow Reactors

Various parallel flow catalysts, including honeycomb, plate, and tube types, have been developed (Figure 3-33). These 50–100 centimeter-long catalysts are placed in containers, transported to the reactor site, and installed as shown in Figure 3-34.

For parallel flow catalysts, "area velocity" (AV) is often used in place of SV (space velocity). It is defined as:

$$AV = \frac{\text{Volume of gas treated (Nm}^3\text{/hr)}}{\text{Apparent surface area of catalyst (m}^2\text{)}}$$

TABLE 3-8. SCR PLANTS USING A MOVING BED REACTOR

| Process Developer | User                 | Plant Site | Gas Source | Fuel             | Capacity (Nm <sup>3</sup> /hr) | Completion |
|-------------------|----------------------|------------|------------|------------------|--------------------------------|------------|
| Kurabo            | Kurabo               | Hirakata   | Boiler     | HO <sup>a</sup>  | 30,000                         | 1975       |
| Asahi Glass       | Asahi Glass          | Keihin     | Furnace    | HO               | 70,000                         | 1976       |
| J.G.C. Corp.      | Catalyst & Chemicals | Wakamatsu  | Furnace    | HO               | 10,000                         | 1976       |
| Mitsubishi H.I.   | Sumitomo Chemical    | Sodegaura  | Boiler     | HO               | 350,000                        | 1976       |
| Hitachi Ltd.      | Kawatetsu Chemical   | Chiba      | Coke Oven  | COG <sup>b</sup> | 500,000                        | 1976       |
| Hitachi Ltd.      | Chiyoda Kenzai       | Kaizuka    | Boiler     | HO               | 15,000                         | 1977       |
| Hitachi Ltd.      | Nisshin Steel        | Amagasaki  | Boiler     | HO               | 19,000                         | 1977       |
| Hitachi Ltd.      | Nippon Oil & Fats    | Amagasaki  | Boiler     | HO               | 20,000                         | 1978       |
| Kobe Steel        | Kansai N.K.          | Amagasaki  | Coke Oven  | COG              | 104,000                        | 1977       |

<sup>a</sup>Heavy oil<sup>b</sup>Coke oven gas

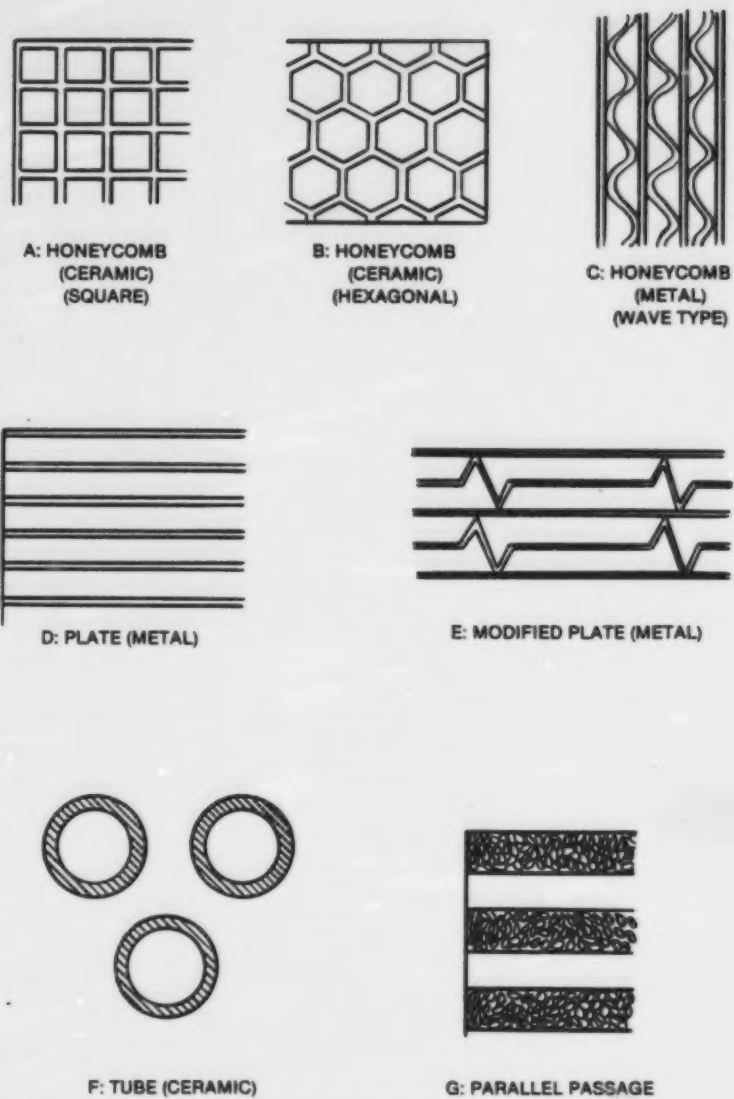


Figure 3-33 Cross-Sections of Parallel Flow Catalysts. (actual size)

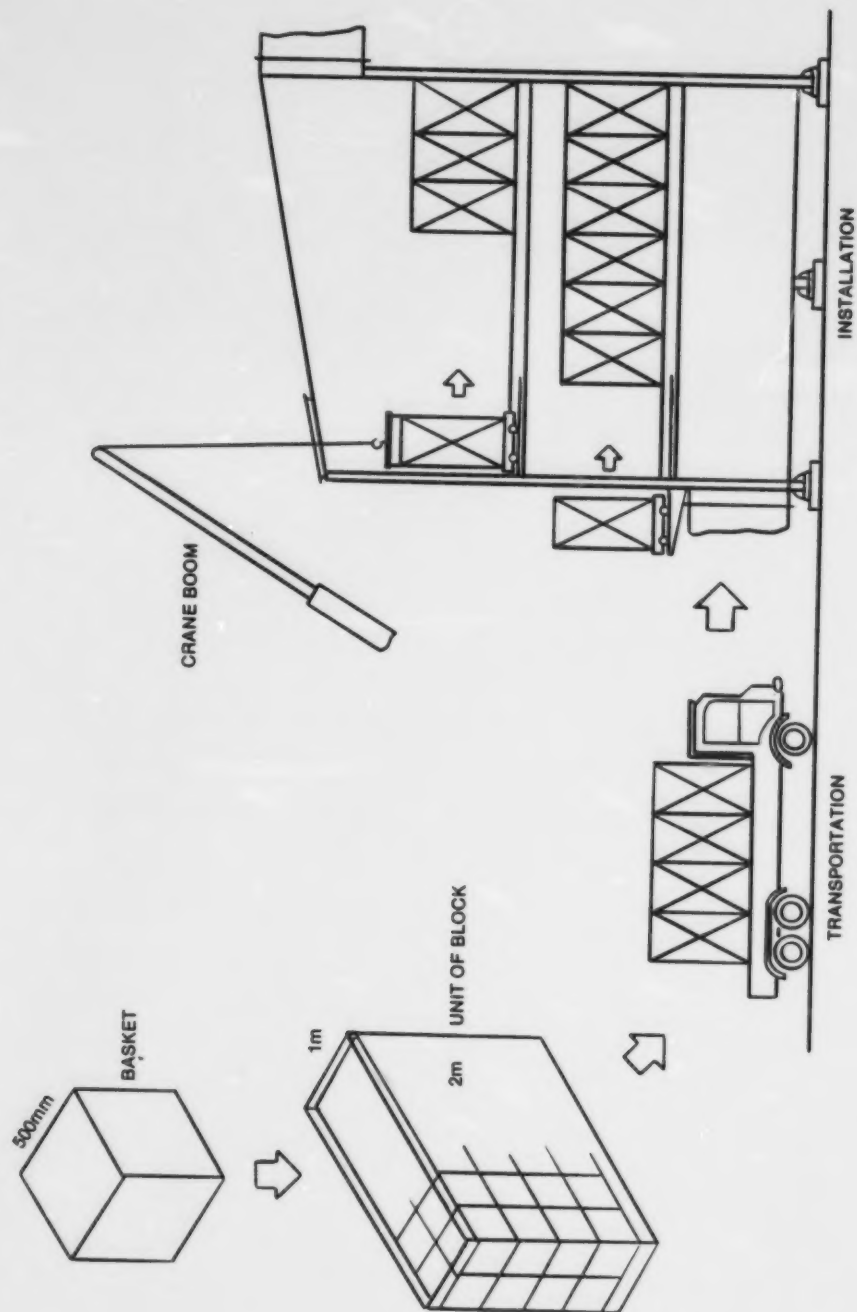


Figure 3-34 Installation of the Catalyst. (Hitachi Ltd.)



Apparent surface area is the surface area assuming that the catalyst surface is smooth, without pores. Examples of the relationship between AV and SV for a square honeycomb catalyst are shown in Table 3-9.

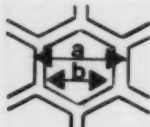
TABLE 3-9. AV AND SV OF SQUARE HONEYCOMB CATALYST

| Channel Diameter<br>(mm) | Wall Thickness<br>(mm) | AV<br>(m/hr) | SV<br>(hr <sup>-1</sup> ) |
|--------------------------|------------------------|--------------|---------------------------|
| 5                        | 1                      | 5            | 2,800                     |
|                          |                        | 10           | 5,600                     |
| 7                        | 1.5                    | 5            | 1,900                     |
|                          |                        | 10           | 3,800                     |
| 10                       | 2                      | 5            | 1,400                     |
|                          |                        | 10           | 2,800                     |

Since the catalytic action occurs on a thin surface layer of the catalyst, a thinner catalyst is more efficient than a thicker one (Table 3-10). Recent technology improvements have made it possible to produce honeycomb and plate catalysts with a thin wall, 0.6-1 mm thick (10). This has resulted in the widespread use of these catalysts, especially for utility boilers (Table 4-1). By comparison, a tube catalyst (Figure 3-33, F) with a length of 100 cm must be more than 2.5 mm thick to have sufficient mechanical strength; it is also a less efficient catalyst. Tube catalysts have been tested with gas containing a large amount of dust, such as the gas from a coal-fired boiler which tends to erode the catalyst.

Another type of parallel flow reactor originally developed by Shell is the parallel passage reactor (Figure 3-33, G). This reactor uses a small catalyst, about 1 mm in diameter and 2-3 mm in length, packed in a 7-8 mm-thick envelope made of steel gauze. The envelopes are placed in parallel in a container with a clearance of 7-9 mm. The catalyst does not need much mechanical strength and thus a very active catalyst can be used. However, inside the envelope, the catalyst may not work as efficiently as it would on the outside surface.

TABLE 3-10. SPECIFIC SURFACE AREA OF CATALYSTS

|                                                                                     |                                   | Specific Surface Area (m <sup>2</sup> /m <sup>3</sup> ) |                               |
|-------------------------------------------------------------------------------------|-----------------------------------|---------------------------------------------------------|-------------------------------|
|                                                                                     |                                   | Surface Area <sup>a</sup><br>Catalyst Volume            | Surface Area<br>Packed Volume |
| Dimension (mm)                                                                      |                                   |                                                         |                               |
|                                                                                     |                                   |                                                         |                               |
| <u>Granule (Sphere)</u>                                                             | <u>Diameter</u>                   |                                                         |                               |
|    | 4                                 | 1500                                                    | 1100                          |
|                                                                                     | 6                                 | 1000                                                    | 740                           |
|                                                                                     | 8                                 | 750                                                     | 555                           |
|                                                                                     | 10                                | 600                                                     | 444                           |
|                                                                                     |                                   |                                                         |                               |
| <u>Tube</u> <sup>c</sup>                                                            | <u>a</u> <u>b</u>                 |                                                         |                               |
|    | 10      7                         | 1350                                                    | 405                           |
|                                                                                     | 15      10.5                      | 900                                                     | 270                           |
|                                                                                     | 20      14                        | 677                                                     | 203                           |
|                                                                                     | 25      17.5                      | 543                                                     | 163                           |
|                                                                                     | 33      23.1                      | 410                                                     | 124                           |
|                                                                                     |                                   |                                                         |                               |
| <u>Honeycomb</u>                                                                    | <u>a</u> <u>b</u>                 |                                                         |                               |
|   | 9      7                          | 1866                                                    | 437                           |
|                                                                                     | 10      7                         | 1204                                                    | 387                           |
|                                                                                     | 14      10                        | 908                                                     | 278                           |
|                                                                                     | 20      14                        | 602                                                     | 193                           |
|                                                                                     |                                   |                                                         |                               |
|                                                                                     | <u>a</u> <u>b</u>                 |                                                         |                               |
|                                                                                     | 7      5                          | 1819                                                    | 556                           |
|                                                                                     | 10      7                         | 1204                                                    | 388                           |
|                                                                                     | 14      10                        | 909                                                     | 277                           |
|                                                                                     | 20      14                        | 601                                                     | 194                           |
|                                                                                     |                                   |                                                         |                               |
| <u>Parallel Plate</u>                                                               | <u>Thickness</u> <u>Clearance</u> |                                                         |                               |
|  | 1              5                  | 2000                                                    | 320                           |
|                                                                                     | 1              8                  | 2000                                                    | 220                           |
|                                                                                     | 8              8                  | 250                                                     | 125                           |
|                                                                                     | 10             12                 | 200                                                     | 91                            |
|                                                                                     |                                   |                                                         |                               |

<sup>a</sup> Apparent surface area.<sup>b</sup> True volume of catalyst assuming that it has no pores.<sup>c</sup> Optimum separate packing.



### 3.4.4 Honeycomb and Plate Catalysts

The composition, production methods, and characteristics of honeycomb and plate catalysts are compared in Table 3-11. The most popular of these catalysts is the solid or molded (C-S) ceramic honeycomb which is produced by kneading, extruding, drying, and calcinating catalyst material such as  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$ . The production process is simple but requires a large amount of material for the honeycomb's relatively thick walls. The thick walls are needed to maintain sufficient mechanical strength.

TABLE 3-11. HONEYCOMB AND PLATE CATALYSTS

| Type                                                                           | Production Method            | Simpliary<br>of<br>Production | Mechanical<br>Strength | Variety of<br>Composition |
|--------------------------------------------------------------------------------|------------------------------|-------------------------------|------------------------|---------------------------|
| <b>Ceramic<br/>Honeycomb</b>                                                   |                              |                               |                        |                           |
| C-S                                                                            | Solid (or molded) type       | A                             | C                      | A                         |
| C-C                                                                            | Ceramic carrier, coated      | B                             | B                      | A                         |
| C-I                                                                            | Ceramic carrier, impregnated | B                             | B                      | B                         |
| <b>Metal Based</b>                                                             |                              |                               |                        |                           |
| M-C                                                                            | Metal plate, coated          | C                             | A                      | A                         |
| MG-C                                                                           | Metal gauze, coated          | B                             | B                      | A                         |
| M-E                                                                            | Metal plate, etched          | B                             | A                      | C                         |
| A = Superior                      B = Medium                      C = Inferior |                              |                               |                        |                           |

The coated ceramic honeycomb (C-C) catalyst has thin walls (0.6-1.2 mm in diameter). To produce the catalyst, a honeycomb substrate (support) with walls 0.3-0.9 mm is formed. The substrate which consists of mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) or cordierite ( $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ) is then coated with 0.15 mm of catalyst material, dried and calcined again. This coated honeycomb has been produced chiefly by NGK Insulators Co., and Kobe Steel. Compared with solid honeycomb, the coated type uses less catalyst material but has greater mechanical strength and a larger surface area, as shown in Figure 3-35.

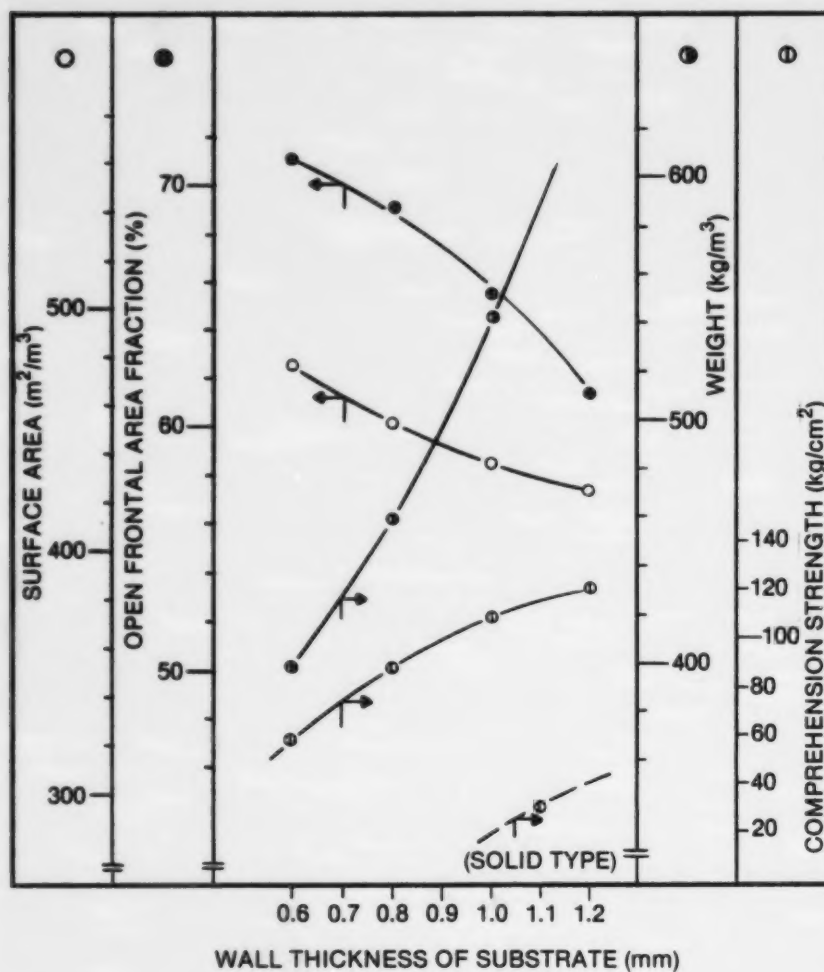


Figure 3-35 Characteristics of Coated Honeycomb Substrate.  
(NGK Insulator Co.)

A third type of ceramic honeycomb is produced by impregnating the ceramic substrate with catalyst material. This type is not popular as an SCR catalyst although it has been widely used for automobile exhaust treatment.

There are also plate or honeycomb catalysts which are produced by coating thin metal plates (M-C) or metal gauze (MG-C) with catalyst material. The thickness of the coating and the metal plate (or gauze) is 0.1-0.2 and 0.3-0.5 mm, respectively. The M-E catalyst is made by etching a special type of stainless steel plate (about 1 mm thick) to produce a reactive 0.15 mm thick surface layer. Honeycomb catalysts made with metal plate (M-C and M-E) may have greater mechanical strength than metal gauze-based and ceramic ones. On the other hand, M-C catalysts need a special cementing material to prevent their coating from coming off during thermal and mechanical shocks; M-E is limited by its chemical composition.

The M-C plate has been produced mainly by Hitachi Ltd., which recently also began manufacturing modified plate catalysts as shown in Figure 3-33, E. To make the modified plate, a stainless steel plate is processed to form wire netting. The netting is treated chemically to prevent SO<sub>2</sub> corrosion, coated for flexibility and formed in the shape of the air preheater element. The M-E catalyst is produced by Hitachi Zosen, which recently began producing the MG-C catalysts as well.

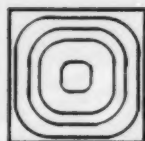
Figure 3-36 shows the gas velocity distribution in each section of a channel of plate and honeycomb type catalysts. The velocity is higher at the center and lower near the wall; it is particularly low in the small-angled corners which are susceptible to dust plugging. Since the honeycomb catalyst has many corners, its efficiency is not substantially higher than that of a plate catalyst although honeycomb does have a larger surface area.

Among the types of honeycomb catalysts, the hexagonal variety is superior to the square or wave types because of its larger corner angles (Figure 3-33). However, the mechanical strength of the hexagonal type is less than that of the square.

EQUILATERAL TRIANGLE



SQUARE



PARALLEL PLATE

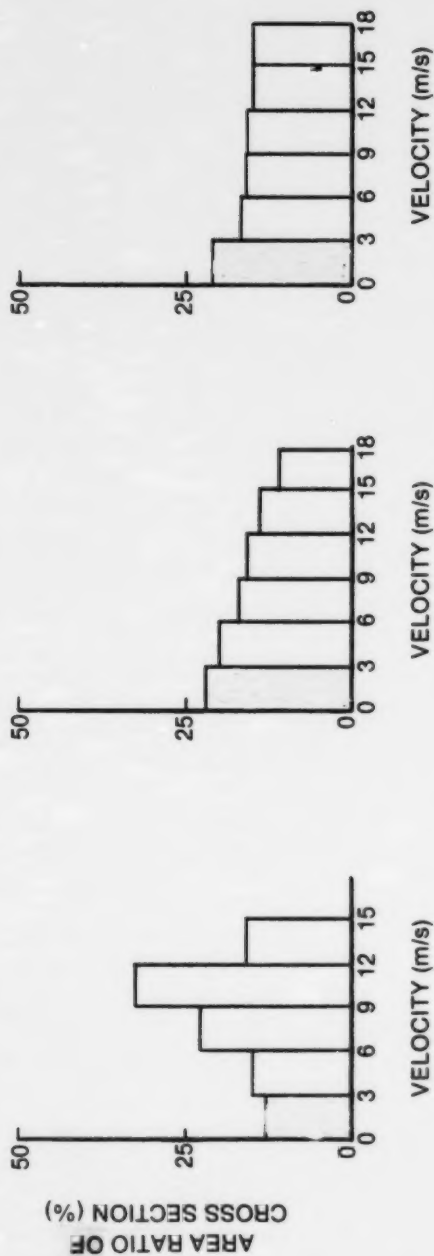


Figure 3-36 Velocity Distribution in Each Section of a Channel of Plate and Honeycomb Catalysts.  
(Hitachi Ltd.)

#### 3.4.5 Comparison of Catalysts and Reactors

The operation parameters and performance of catalysts and reactors are compared in Tables 3-12 and 3-13. A moving bed reactor has a thin catalyst bed through which a low velocity gas passes in order to minimize pressure drop. Parallel flow reactors have much deeper beds and much higher gas velocities. With parallel flow catalysts, especially those with large channel diameters, a low gas velocity produces a low  $\text{NO}_x$  removal efficiency due to the laminar flow of the gas. Moreover, particulates tend to adhere to the catalyst at a low gas velocity thereby reducing catalytic activity (Figure 3-37). A high gas velocity causes a turbulent flow, reduces particulate adhesion and increases  $\text{NO}_x$  removal efficiency (Figure 3-37, B). On the other hand, a high velocity also increases the pressure drop and the catalytic erosion caused by particulates. Therefore, it is best to use a moderate gas velocity with an appropriate channel diameter and bed depth suited to the  $\text{NO}_x$  removal efficiency required, dust content of the gas, fan capacity, etc.

As shown in Tables 3-12 and 3-13, a moving bed reactor can have a larger SV than a parallel flow reactor. The moving bed reactors have not been widely used because of their higher pressure drop and the possibility of mechanical problems including catalyst attrition. Parallel flow reactors have no moving parts and this allows unattended operation. Both honeycomb and plate catalysts with thin walls are most commonly used because of their high efficiency and low pressure drop.

A particular catalyst and reactor should be chosen according to the composition of the gas to be cleaned, nature of the dust, desired  $\text{NO}_x$  removal efficiency, catalyst life, and other factors.



TABLE 3-12. COMPARISON OF CATALYSTS AND REACTORS<sup>a</sup>

| Catalyst size (mm)                               | Moving bed | Ceramic |         | Honeycomb or Plate Metal Base | Tube  | Parallel Passage |
|--------------------------------------------------|------------|---------|---------|-------------------------------|-------|------------------|
|                                                  |            | Molded  | Coated  |                               |       |                  |
| Diameter                                         | 5-7        |         |         |                               |       |                  |
| Wall thickness                                   |            | 1-2     | 0.6-1.2 | 0.5-1                         | 3-5   | 7-9 <sup>e</sup> |
| Channel diameter                                 |            | 5-8     | 4-8     | 4-8                           | 15-30 | 7-9              |
| Gas Velocity (m/sec) <sup>b</sup>                | 0.5-1.5    | 3-7     | 3-7     | 3-7                           | 5-10  | 5-10             |
| Bed depth (m)                                    | 0.3-0.6    | 1.5-3.5 | 1.2-3   | 1.2-3                         | 3-5   | 3-5              |
| SV (1000 hr <sup>-1</sup> ) <sup>c</sup>         | 5-8        | 3-6     | 3.5-7   | 3.5-7                         | 2-4   | 2.5-5            |
| Pressure drop (mm H <sub>2</sub> O) <sup>d</sup> | 50-90      | 20-60   | 15-50   | 15-40                         | 50-90 | 50-90            |

<sup>a</sup>80-85% NO<sub>x</sub> removal with an NH<sub>3</sub>/NO<sub>x</sub> mole ratio of 0.85-0.9 at 350-400°C for dirty gas. (SO<sub>x</sub>: 200-2000 ppm. Particulates: 0.02-0.2 g/Nm<sup>3</sup> for moving bed and 0.02-20 g/Nm<sup>3</sup> for others.)

<sup>b</sup>Velocity at 350-400°C in open column (superficial velocity)

<sup>c</sup>Gas volume (Nm<sup>3</sup>/hr)/catalyst volume (m<sup>3</sup>)

<sup>d</sup>By catalyst bed

<sup>e</sup>Thickness of envelope

TABLE 3-13. TYPICAL EXAMPLES OF SCR FOR BOILER FLUE GASES (350°C, Leak NH<sub>3</sub> 5-10 ppm)

| Fuel              | Dust<br>(g/Nm <sup>3</sup> ) | Inlet<br>NO <sub>x</sub><br>(ppm) | NO <sub>x</sub><br>Removal<br>(%) | NH <sub>3</sub> /NO <sub>x</sub><br>mole<br>Ratio | Granular Catalyst                |                           |                                                        |                           | Honeycomb Catalyst <sup>d</sup> |                           |                           |                                                        |
|-------------------|------------------------------|-----------------------------------|-----------------------------------|---------------------------------------------------|----------------------------------|---------------------------|--------------------------------------------------------|---------------------------|---------------------------------|---------------------------|---------------------------|--------------------------------------------------------|
|                   |                              |                                   |                                   |                                                   | Diameter<br>(mm)                 | SV<br>(hr <sup>-1</sup> ) | Pressure<br>Drop<br>(mm H <sub>2</sub> O) <sup>f</sup> | SV<br>(hr <sup>-1</sup> ) | Channel<br>Diameter<br>(mm)     | Wall<br>Thickness<br>(mm) | SV<br>(hr <sup>-1</sup> ) | Pressure<br>Drop<br>(mm H <sub>2</sub> O) <sup>f</sup> |
| Gas               | 0-0.01                       | 100                               | 80<br>90                          | 0.90<br>1.00                                      | 5 <sup>d</sup><br>5 <sup>d</sup> | 18,000<br>13,500          | 50<br>65                                               |                           | 5<br>5                          | 1.2<br>1.2                | 9,500<br>7,000            | 30<br>40                                               |
| Oil<br>(low)      | 0.01-0.05                    | 100                               | 80<br>90                          | 0.90<br>1.00                                      | 5 <sup>e</sup><br>5 <sup>e</sup> | 11,000<br>8,000           | 70<br>85                                               |                           | 6<br>6                          | 1.4<br>1.4                | 5,300<br>3,800            | 40<br>50                                               |
|                   |                              | 200                               | 80<br>90                          | 0.86<br>0.96                                      | 5 <sup>e</sup><br>5 <sup>e</sup> | 9,000<br>6,500            | 80<br>95                                               |                           | 6<br>6                          | 1.4<br>1.4                | 4,700<br>3,300            | 45<br>55                                               |
| Oil<br>(high)     | 0.05-0.2                     | 200                               | 80<br>90                          | 0.86<br>0.96                                      | 5 <sup>f</sup><br>5 <sup>f</sup> | 7,000<br>5,000            | 90<br>105                                              |                           | 7<br>7                          | 1.6<br>1.6                | 3,600<br>2,500            | 50<br>60                                               |
| Coal <sup>a</sup> | 0.05-0.2                     | 300                               | 80<br>90                          | 0.85<br>0.95                                      | 5 <sup>f</sup><br>5 <sup>f</sup> | 6,500<br>4,500            | 95<br>110                                              |                           | 7<br>7                          | 1.6<br>1.6                | 3,300<br>2,200            | 50<br>60                                               |
| Coal <sup>a</sup> | 15-25                        | 300                               | 80<br>90                          | 0.85<br>0.95                                      | Not feasible                     |                           |                                                        |                           | 8<br>8                          | 1.8<br>1.8                | 2,700<br>1,800            | 55<br>80                                               |

<sup>a</sup> Flue gas is passed through a hot-side ESP prior to SCR.<sup>b</sup> Flue gas with full dust load is treated by SCR.<sup>c</sup> Pressure drop through catalyst bed<sup>d</sup> Fixed bed<sup>e</sup> Intermittent moving bed<sup>f</sup> Continuous moving bed



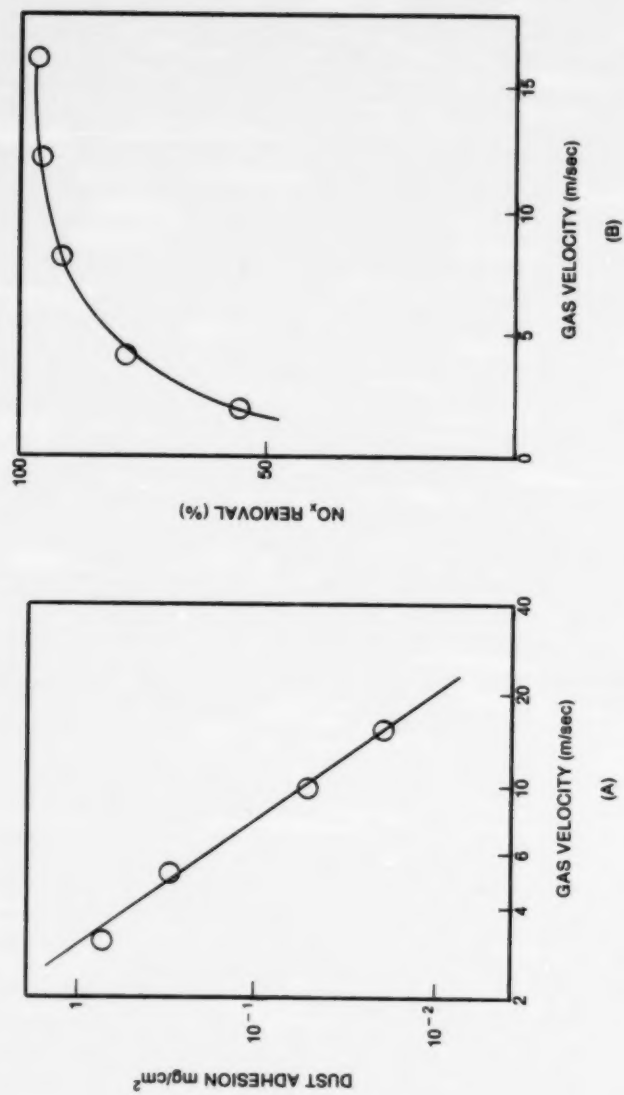


Figure 3-37 Results of a Test Using a Honeycomb Catalyst with Flue Gas Containing 380 mg/Nm<sup>3</sup> of Fly Ash.

### 3.5 PROBLEMS WITH SCR FOR COAL-FIRED BOILERS

#### 3.5.1 Introduction

The application of SCR to flue gas from coal-fired boilers has become more and more important in Japan because of the increase in the number of coal-fired boilers and the relatively high  $\text{NO}_x$  concentration in their flue gas --- 200-400 ppm (depending on coal and furnace types) even with advanced combustion modification. Table 3-14 lists commercial SCR plants for coal-fired boilers.

SCR for coal-fired boiler flue gas has had the following problems:

- (1) When coal-fired utility boilers use pulverized coal, the flue gas contains 15-25 g/ $\text{Nm}^3$  of fly ash. This fly ash is made up of hard spherical particles (1-30 microns in diameter) which erode the catalysts.
- (2) Adhesion of the fly ash to the catalyst causes a decrease in catalytic activity as well as plugging of the catalyst.
- (3) A low-oxidation catalyst may be needed because the flue gas is usually rich in  $\text{SO}_2$ .
- (4) The fly ash may become contaminated by ammonium compounds which may present problems with the utilization and disposal of the ash (Section 3.7.2).

There are two SCR systems available for the treatment of flue gas--- high-dust and low-dust, as shown in Figure 3-38. In the high-dust system, economizer outlet gas with a full dust load is passed through an SCR reactor, air preheater, and then a cold-side electrostatic precipitator (cold ESP) or baghouse. In the low-dust system, the economizer outlet gas is first treated with a hot-side ESP (hot ESP) to reduce the dust content to 50-200 mg/ $\text{Nm}^3$

TABLE 3-14. COMMERCIAL SIZE PLANTS FOR COAL-FIRED BOILERS IN JAPAN

| Power Company        | Power Station | Capacity<br>(Hw) | H/R            | Manufac-<br>turer | Catalyst       | Year of<br>Completion | High Dust<br>or Low Dust | NO <sub>x</sub> Removal %<br>(Design) |
|----------------------|---------------|------------------|----------------|-------------------|----------------|-----------------------|--------------------------|---------------------------------------|
| Chugoku Electric     | Shimonoseki   | 175              | R <sup>a</sup> | MHI <sup>c</sup>  | H <sup>b</sup> | 1980                  | High                     | 55 <sup>k</sup>                       |
| "                    | Shin Ube      | 75               | R              | MHI               | H              | 1982                  | High                     | 65 <sup>k</sup>                       |
| "                    | Shin Ube      | 75               | R              | MHI               | H              | 1982                  | High                     | 65 <sup>k</sup>                       |
| "                    | Shin Ube      | 156              | R              | MHI               | H              | 1982                  | High                     | 65 <sup>k</sup>                       |
| "                    | Mizushima     | 125              | R              | BH <sup>d</sup>   | P <sup>h</sup> | 1984                  | High                     | 65 <sup>k</sup>                       |
| "                    | Mizushima     | 156              | R              | BH                | P              | 1984                  | High                     | 65 <sup>k</sup>                       |
| Electric Power D.C.  | Takehara      | 250 x 1/2        | R              | BH                | P              | 1981                  | Low                      | 80                                    |
| "                    | Takehara      | 250 x 1/2        | R <sup>b</sup> | KHI <sup>e</sup>  | T <sup>i</sup> | 1981                  | Low                      | 80                                    |
| "                    | Takehara      | 700              | N <sup>a</sup> | BH                | P              | 1983                  | Low                      | 80                                    |
| Hokkaido Electric    | Tomato        | 350 x 1/2        | N              | BH                | P              | 1980                  | Low                      | 80                                    |
| Joban Kyodo Electric | Nakoso        | 600              | N              | MHI <sup>f</sup>  | H              | 1982                  | High                     | 80                                    |
| "                    | "             | 600              | N              | MHI               | H              | 1983                  | High                     | 80                                    |
| Kyushu Electric      | Minato        | 156              | R              | MHI               | H              | 1983                  | High                     | 50 <sup>k</sup>                       |
| Tohoku Electric      | Sendai        | 175              | R              | BH                | P              | 1982                  | High                     | 56 <sup>k</sup>                       |
| Tohoku Electric      | Sendai        | 175              | R              | BH                | P              | 1982                  | High                     | 56 <sup>k</sup>                       |

<sup>a</sup> Retrofit<sup>b</sup> New<sup>c</sup> Mitsubishi Heavy Industries<sup>d</sup> Babcock Hitachi<sup>e</sup> Kawasaki Heavy Industries<sup>f</sup> Ishikawajima-Harima Heavy Industries<sup>g</sup> Honeycomb<sup>h</sup> Plate<sup>i</sup> Tube<sup>k</sup> Reactor is designed for 80% removal, which is attained by increasing the amount of catalyst

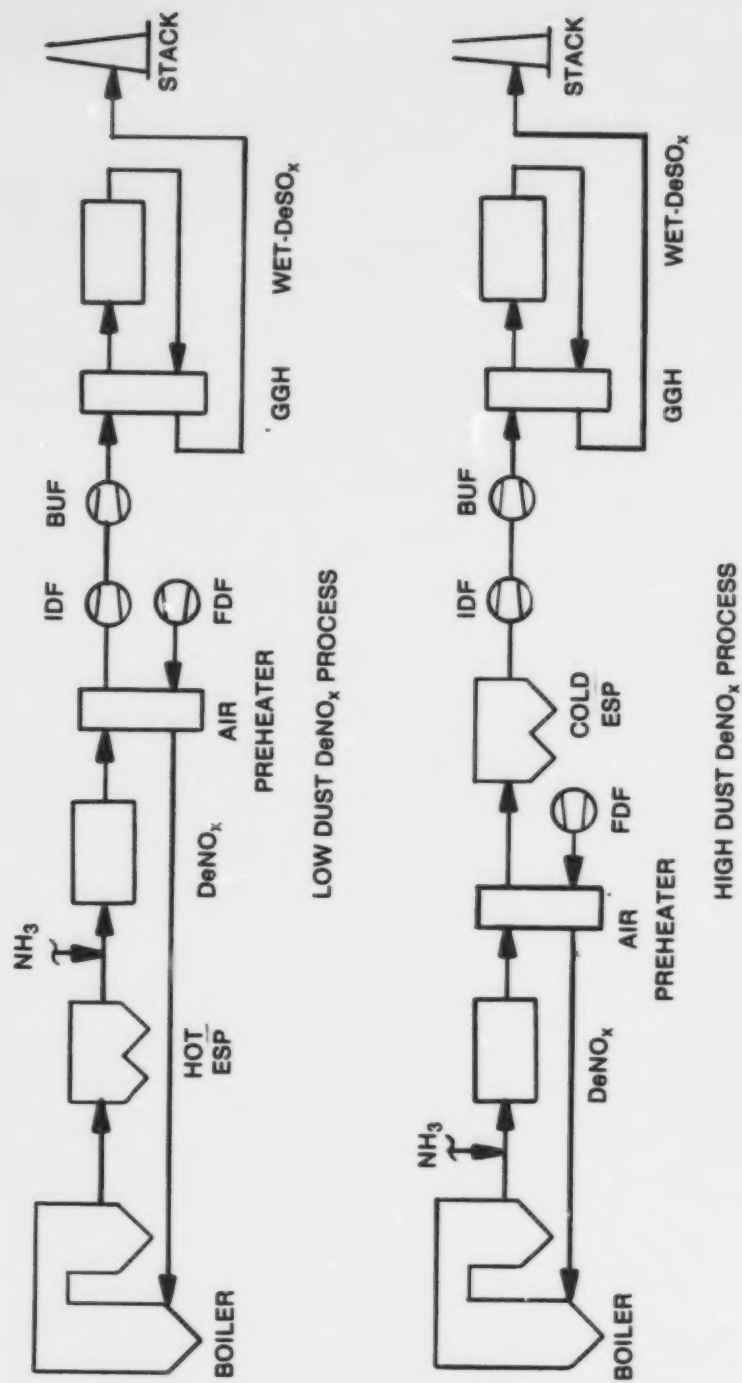


Figure 3-38 Total Flue Gas Treatment Process for Coal-Fired Boilers.

(over 99% removal) and then passed through an SCR reactor and an air preheater.

The advantages and disadvantages of the high-dust and low-dust systems are compared in Table 3-15.

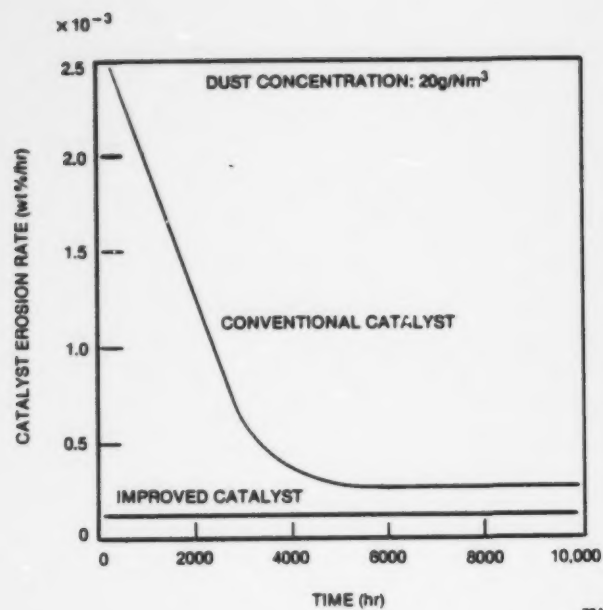
TABLE 3-15. COMPARISON OF HIGH-DUST AND LOW-DUST SCR SYSTEMS FOR COAL

|                                                | High-Dust System                                     | Low-Dust System             |
|------------------------------------------------|------------------------------------------------------|-----------------------------|
| Catalyst erosion by dust                       | More                                                 | Less                        |
| Dust adhesion to catalyst                      | Less                                                 | More                        |
| Ammonium bisulfate deposition in air preheater | Less                                                 | More                        |
| Contamination of fly ash by ammonium compounds | Can be prevented by reducing unreacted $\text{NH}_3$ | None                        |
| Cost of ESP                                    | Less                                                 | More                        |
| Nature of ESP                                  | Suitable to medium and high sulfur coals             | Suitable to low sulfur coal |

With the low-dust system, catalyst erosion does not occur but the dust leaving the hot ESP consists of fine, relatively alkaline ash which tends to adhere to the surface of the catalyst. In addition, ammonium bisulfate deposits tend to form in the air preheater. With the high-dust system the large amount of dust prevents the deposit of bisulfate. On the other hand, fly ash caught by the cold ESP may contain a noticeable amount of ammonium compounds, which can cause problems in utilizing or disposing of the ash. Both high-dust and low-dust systems have been used commercially in Japan (Table 3-15). The high-dust system may prove to have more advantages than the low-dust system if the problem of ammonia contamination of the fly ash can be solved (Section 3.7).

### 3.5.2 Fly Ash Erosion of the Catalyst

With a parallel flow catalyst, erosion occurs mainly at the gas inlet and, to a lesser degree, on the inside surfaces. Figure 3-39 compares the

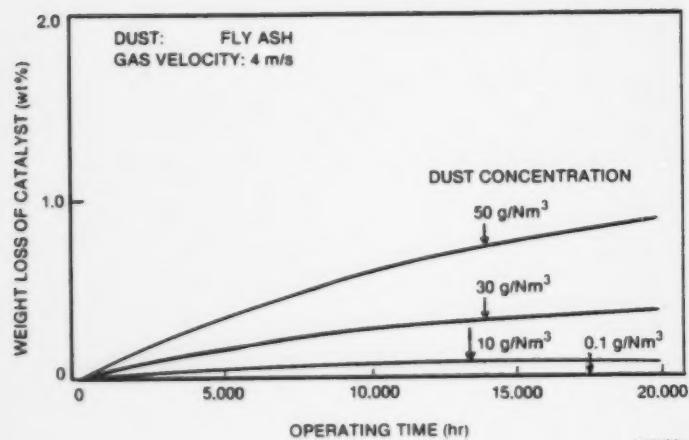


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Figure 3-39 Change in Catalyst Erosion Rate with Time. (6)

EXPERIMENTAL EQUATION  
 $W = K \cdot V^{2.9} \cdot C^{1.7} \cdot T^{0.64}$

W: WEIGHT LOSS OF CATALYST (wt%)  
 K: CONSTANT  
 V: GAS VELOCITY (m/s)  
 C: DUST CONCENTRATION (g/Nm<sup>3</sup>)  
 T: OPERATING TIME (hr)



70A2734

Figure 3-40 Anticipated Weight Loss of Plate Catalyst vs. Operating Time. (2)



erosion rates of conventional and improved tube catalysts (6). With the conventional molded catalyst a substantial amount of erosion occurs at the beginning of operation and then continues slowly. The erosion can be significantly reduced by hardening as much as 1/100 to 1/50 of the length of the inlet portion of the catalyst by impregnation with a certain material (6).

Figure 3-40 shows the weight loss in a metal-based plate catalyst that is caused by fly ash erosion (2). The figure indicates that as far as erosion is concerned, the catalyst may be useful for over 2 years; the weight loss in 20,000 hours is about 0.3% with flue gas containing 30 g/Nm<sup>3</sup> of dust at a velocity of 4 m/sec. The figure also shows an empirical equation which explains the relationship between the weight loss and the gas velocity, dust concentration, and operation time. The equation indicates that the weight loss associated with a flue gas (velocity: 6 m/sec) containing 20 g/Nm<sup>3</sup> of dust is about 0.5% in 20,000 hours.

Figure 3-41 compares the erosion ratio of different types of honeycomb catalysts (7). A conventional molded catalyst D is most susceptible to erosion, while catalyst C, which contains an impregnated catalyst carrier, undergoes less erosion because of the hardness of the carrier. Catalyst B, which contains erosion-resistant material, undergoes even less erosion. In the case of the improved catalyst B (B and dummy), erosion was eliminated altogether by using a dummy layer which has the same cross section as the catalyst and is placed upstream of it to absorb the impact and act as a flow straightener.

### 3.5.3 Dust Adhesion and Plugging

Fly ash from pulverized coal usually consists of spherical particles of a hard glassy substance. The particles are generally 1-30 microns in diameter and have fairly smooth surfaces as shown in Figure 3-42. Therefore, the dust adhesion and plugging problem can be eliminated when a flue gas with full dust load is sent down through parallel flow catalysts with a sufficient channel diameter. An excessively high gas velocity can cause the catalyst to erode and a large channel diameter makes the process less efficient. A gas velocity



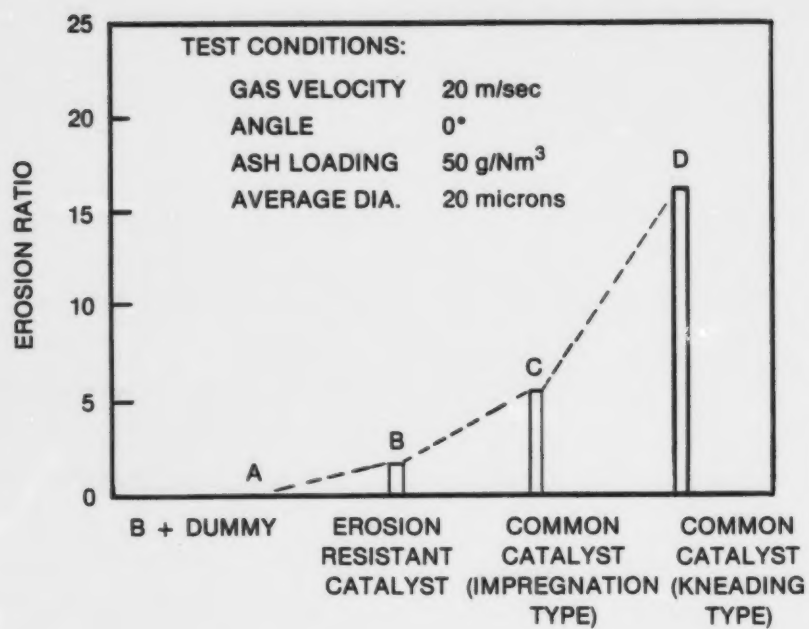
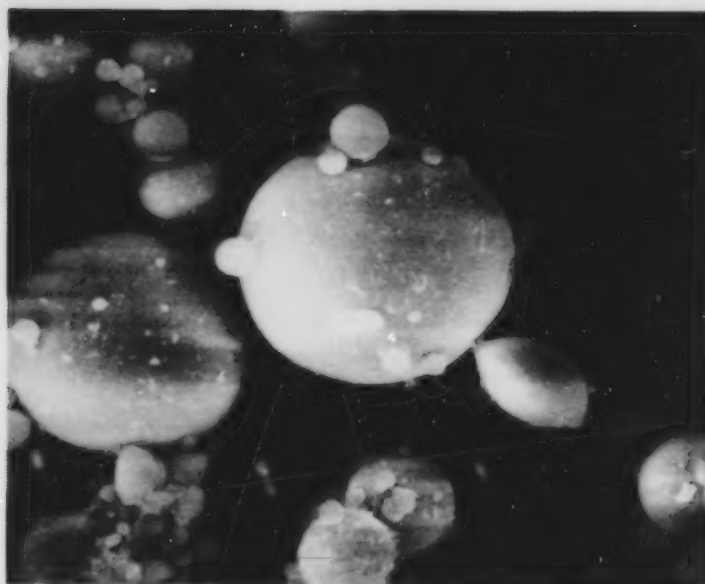
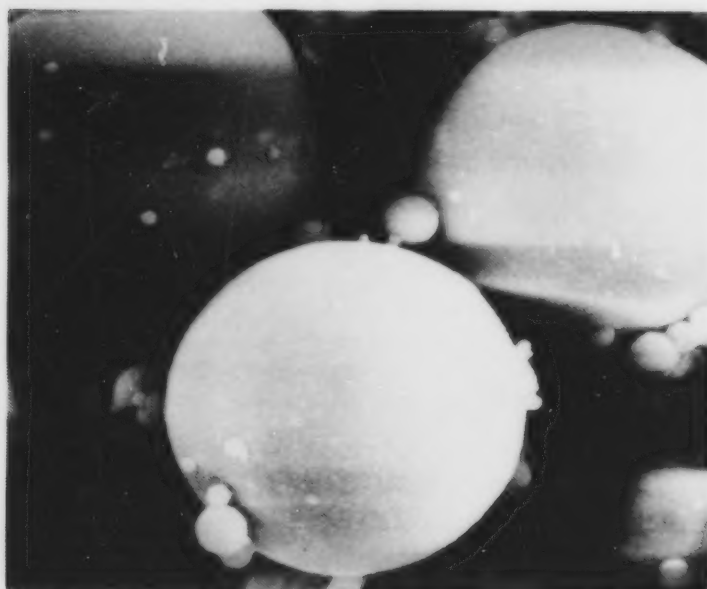


Figure 3-41 Results of Accelerated Erosion Test. (7)



(A) TAKASAGO (MEDIUM-SULFUR COAL)



(B) ISOGO (LOW-SULFUR COAL)

**Figure 3-42** Fly Ash From Coal-Fired Boilers In Japan  
(Japanese Coals) (x3000)

around 5 m/sec and a channel diameter of 5-8 mm for honeycomb, or clearance of 4-7 mm for the plate catalyst, are usually used to eliminate these problems.

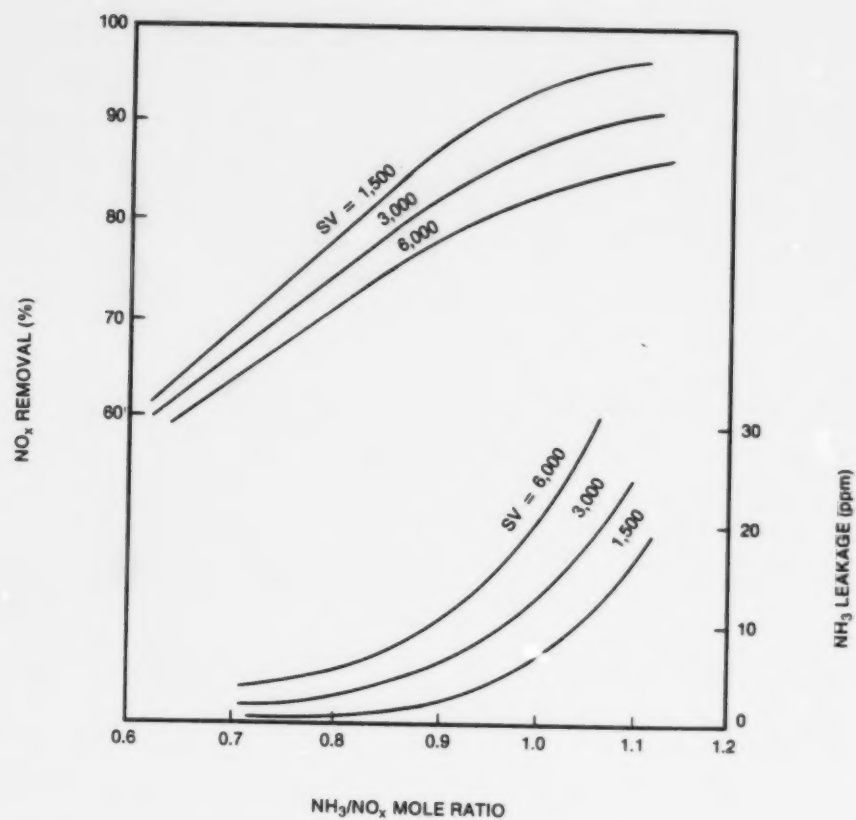
On the other hand, the fly ash leaving a hot ESP consists mainly of smaller particles which are often rich in alkaline components and have a tendency to adhere to the catalyst surface, especially at the gas inlet. Since the amount of ash leaving the hot ESP is not large, the dust adhesion and plugging problem can be eliminated by occasional soot blowing.

The design and operation of SCR plants for coal-fired boilers in Japan have been improved significantly so that there is generally no dust clogging problem with the catalyst, even without soot blowing. The U.S. Environmental Protection Agency (EPA) conducted SCR demonstration tests with Hitachi Zosen's honeycomb catalyst at Georgia Power's Mitchell Pilot Plant. Results of this test showed that the fly ash adhered considerably on the catalyst surface even with soot blowing, resulting in a decrease in  $\text{NO}_x$  removal efficiency and/or an increase in the pressure drop. Although the adhesibility might be caused by a unique condition at the pilot plant (Section 4.10.3) further studies are needed on the adhesive properties of fly ash with different compositions.

It may not be feasible to use SCR on plants fired with coal if a considerable portion of the alkali compounds are volatilized by combustion. The alkali components may condense on the catalyst and poison it to some extent.

#### 3.5.4 $\text{NO}_x$ Removal Efficiency for Flue Gas from Coal

An example of SCR for coal-fired boiler flue gas using a honeycomb catalyst is shown in Figure 3-43. Generally speaking, the amount of catalyst needed for coal-fired boilers is about twice the amount needed for low-sulfur oil-fired boilers with equal power generation capacities. This is true for the following reasons: 1) Flue gas volume is nearly 20% more for coal than for oil given an equal power generation capacity. 2) Because of a higher  $\text{SO}_2$  concentration in the coal flue gas, a less active low-oxidation catalyst is needed. 3) Since a large amount of fly ash in coal flue gas tends to cause erosion, the catalyst has to be harder and less active. 4) In order to



(channel diameter: 8mm; wall thickness: 1.8mm; inlet  $\text{NO}_x$ : 300 ppm;  
full dust load; pilot plant test)

Figure 3-43 SCR for Coal-Fired Boiler Flue Gas at 350°C Using Honeycomb Catalyst.

prevent dust plugging, a larger channel diameter is needed (Table 3-13). 5) Higher inlet  $\text{NO}_x$  concentrations require a larger amount of the catalyst for a given  $\text{NO}_x$  removal ratio with a given concentration of unreacted  $\text{NH}_3$  (Figure 3-4).

In order to prevent the plugging of the air preheater with ammonium bisulfate (Section 3.6), it is necessary to keep unreacted  $\text{NH}_3$  below 10 ppm for the high-dust system and below 5 ppm for the low-dust system. For the high-dust system, it may be necessary to maintain the unreacted  $\text{NH}_3$  level below 5 ppm in order to eliminate the contamination of fly ash by ammonium compounds.

Figure 3-43 indicates that a 90 percent  $\text{NO}_x$  removal efficiency with an unreacted  $\text{NH}_3$  level below 5 ppm may be attained with the  $\text{NH}_3/\text{NO}_x$  mole ratio of 0.93 and an SV of  $1,500 \text{ hr}^{-1}$ . When treating a large amount of flue gas from a utility boiler, it may be difficult to attain 90 percent removal with 5 ppm unreacted  $\text{NH}_3$  for two reasons. First, the flue gas velocity as well as  $\text{NO}_x$  concentration is not uniform in each portion of the large inlet duct and reactor, and second, boiler load often fluctuates, resulting in the fluctuation of the gas volume and  $\text{NO}_x$  concentration. In order to maintain unreacted  $\text{NH}_3$  below 5 ppm, an 80-85 percent  $\text{NO}_x$  removal efficiency may be a practical limit for a large coal-fired boiler.

### 3.6 AMMONIUM BISULFATE DEPOSITION IN THE AIR PREHEATER

#### 3.6.1 Formation and Behavior of Ammonium Bisulfate

While most problems with SCR already have been solved, the greatest remaining problem is the deposit of ammonium bisulfate in the air preheater or heat exchanger causing plugging and corrosion (Figure 3-44). The problem is significant, not only for SCR but also for selective noncatalytic reduction (SNR or Thermal  $\text{DeNO}_x$ ) as well.

$\text{SO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  present in hot gas combine to form ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ), on cooling:



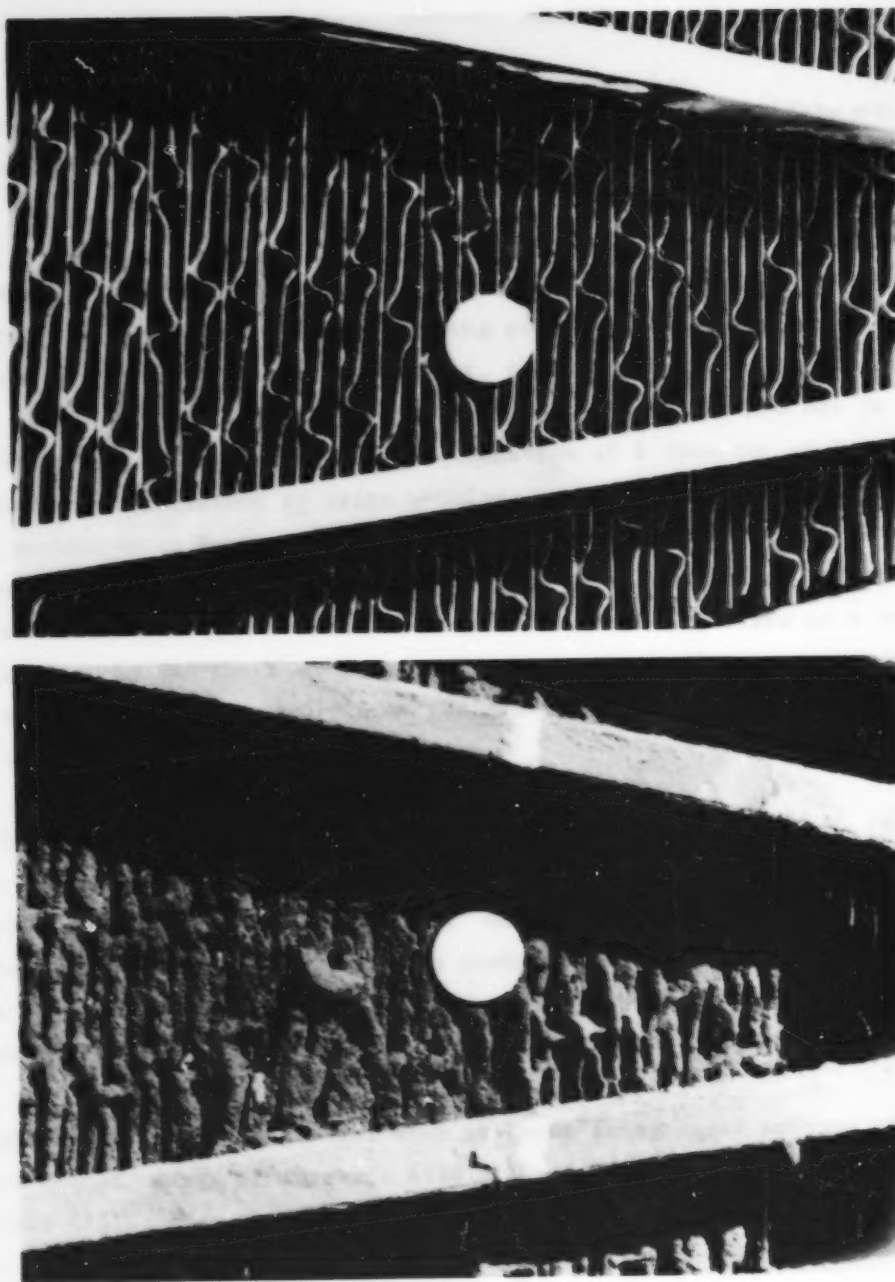
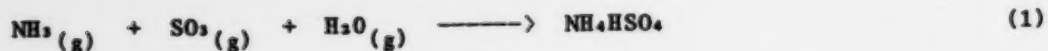


**Figure 3-44**    **Air Preheater Elements: Clean (Above)**  
**Plugged (Below)**



The formation temperature is shown in Figure 3-45. Bisulfate will form below approximately 230° C in a gas containing about 10 ppm of both  $\text{NH}_3$  and  $\text{SO}_3$ .

Ammonium bisulfate has a melting point of 147°C (Figure 3-46). Between the formation temperature and the melting point, bisulfate exists as a corrosive melt. Below the melting point, it exists as a very hygroscopic solid. A simple calculation shows that 10 ppm each of  $\text{SO}_3$  and  $\text{NH}_3$  in gas from a 500 MW boiler could account for the formation of 2 tons/day of bisulfate. This amount is sufficient to cause problems such as plugging and corrosion in an air preheater or heat exchanger. Many problems of this nature have been encountered in a few SCR facilities in Japan. The problem has not been as serious for small boilers and furnaces that discharge flue gas at a temperature above about 230°C. However, for larger boilers and furnaces which require sufficient heat recovery from the flue gas, countermeasures must be taken to eliminate the bisulfate problem.

There is some question about the composition of the substance which first forms. Based on thermodynamic data, it appears that ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , deposits from  $\text{NH}_3$ -rich gas. However, the sulfate may not be stable at a high temperature. This author's study indicates that  $(\text{NH}_4)_2\text{H}(\text{SO}_4)_3$ , a double salt of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ , forms at a high temperature under the presence of excessive  $\text{NH}_3$  (16).

Other studies indicate that when gas containing equal amounts of  $\text{SO}_3$  and  $\text{NH}_3$ , is cooled, mists of sulfuric acid  $\text{H}_2\text{SO}_4$  form prior to the formation of bisulfate (13). Even though the mists form, they must absorb ammonia immediately, according to the  $\text{NH}_3$  concentration. When a hot gas cools, the result may be the formation of mists with varying compositions based on the gas composition. The mists solidify either partly or entirely on further cooling to form a mixture of sulfuric acid and ammonium bisulfate, bisulfate and double salt, or double salt and ammonium sulfate as will be shown in Section 3.6.3.



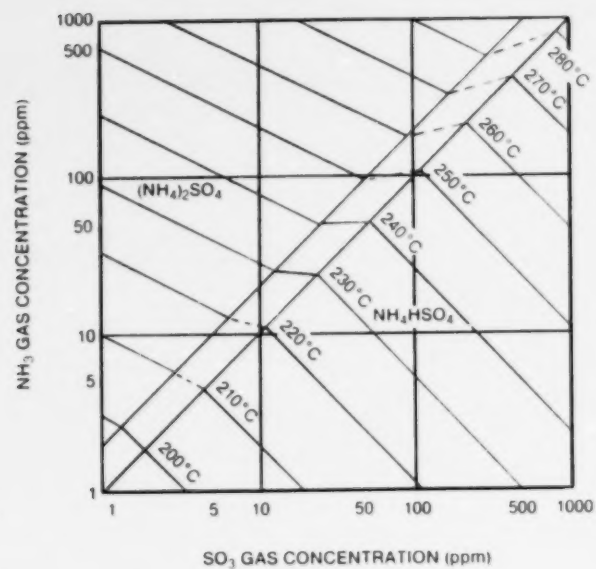


Figure 3-45 Formation Temperature of Ammonium Sulfate and Bisulfate. (12)

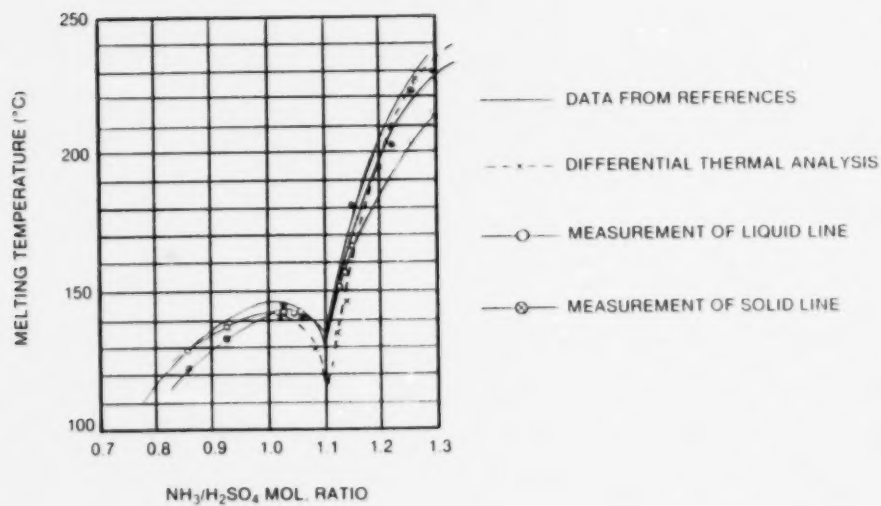


Figure 3-46 Melting Point of  $\text{NH}_3$ - $\text{H}_2\text{SO}_4$  System. (12)

Bisulfate, particularly when combined with sulfuric acid, is highly corrosive and readily reacts with air preheater material and fly ash to form various solid compounds (Sections 3.6.6 and 3.6.7). The reaction products also cause plugging of the air preheater.

It should be noted that although the formation of compounds causes problems, at the same time it helps to reduce  $\text{SO}_3$  emissions. Sulfuric acid mists are far more hazardous than  $\text{SO}_2$  and yet are not well captured with FGD. Ammonium promotes deposit formation and prevents the emission of  $\text{SO}_3$  or sulfuric acid mists.

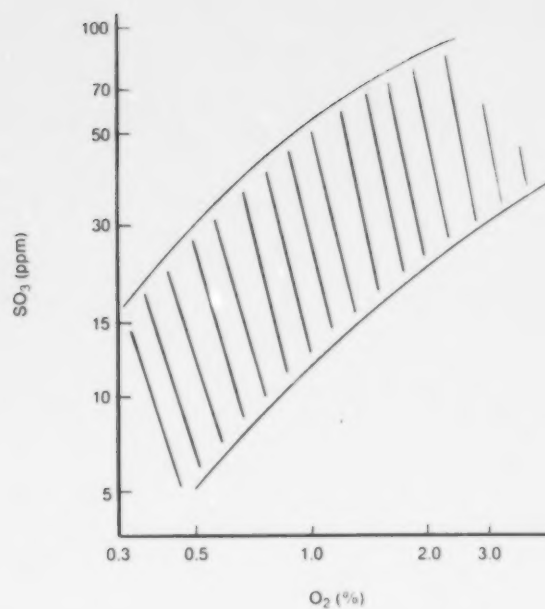
### 3.6.2 Formation of $\text{SO}_3$

The relationship of  $\text{SO}_3$  and  $\text{O}_2$  concentrations in flue gas from the combustion of heavy oil is shown in Figure 3-47. The figure indicates that  $\text{SO}_3$  increases with an increase in the  $\text{O}_2$  concentration in the gas. Therefore, low-oxygen combustion to reduce  $\text{NO}_x$  also helps to reduce  $\text{SO}_3$ . The use of less oxygen, however, tends to increase the particulate content; particulates increase as  $\text{SO}_3$  decreases, as shown in Figure 3-48. Usually 1-3 percent of the total  $\text{SO}_x$  in flue gas from heavy oil is present as  $\text{SO}_3$  under good combustion conditions. It has been shown that the  $\text{SO}_3$  concentration in gas from coal is lower than that in gas from heavy oil. This is because coal fly ash is a better adsorbent of  $\text{SO}_3$ .

The catalyst for selective catalytic reduction of  $\text{NO}_x$  oxidizes a small portion of  $\text{SO}_2$  to  $\text{SO}_3$ . The actual oxidation ratio differs with catalyst composition, temperature, and  $\text{O}_2$  and  $\text{NH}_3$  concentrations (Section 3.2.4). Although catalysts with a low oxidation ratio (below 1%) can be used, a considerable amount of  $\text{SO}_3$  still may form in  $\text{SO}_2$ -rich gas.

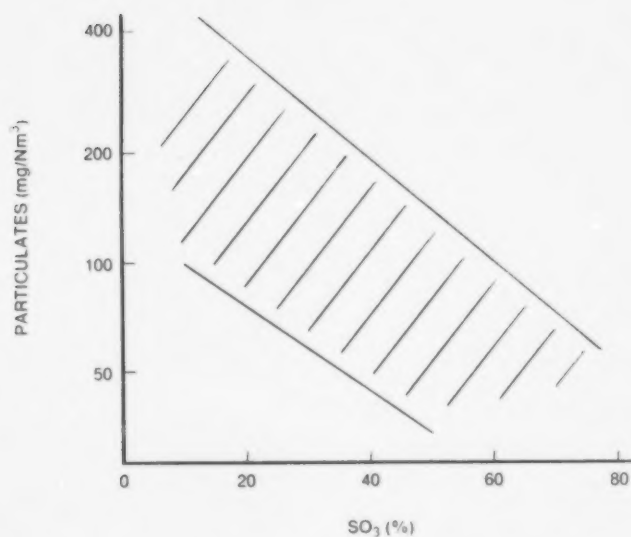
### 3.6.3 Laboratory Tests on Bisulfate Deposition (12)

Figures 3-49 and 3-50 show an apparatus used to test ammonium bisulfate deposition. Gases containing  $\text{NH}_3$ ,  $\text{SO}_3$ , and  $\text{H}_2\text{O}$ , are preheated and mixed at  $400^\circ\text{C}$ , and then sent through connected pyrex glass tubes 9.5 mm in inner



(heavy oil, S:1.3%) (14)

Figure 3-47 Relationship of  $\text{O}_2$  and  $\text{SO}_3$  Concentrations.



(heavy oil, S:1.3%;  $\text{O}_2$  in gas: 0.3-3%) (14)

Figure 3-48 Relationship of  $\text{SO}_3$  Concentration to Particulate Content.

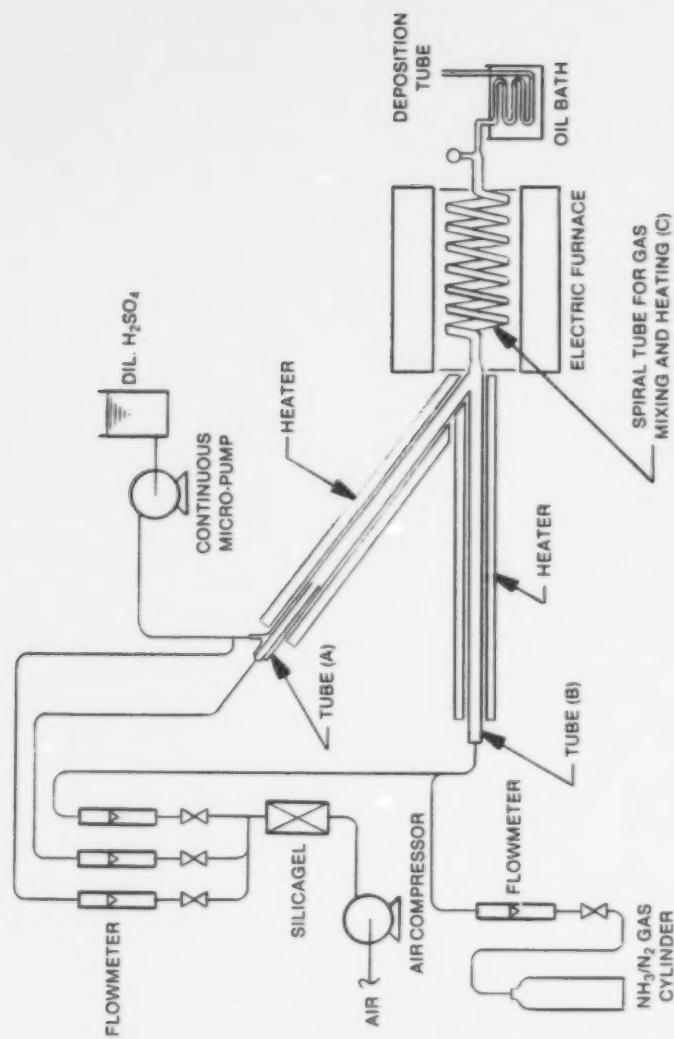


Figure 3-49 Apparatus for Ammonium Bisulfate Deposition Test.

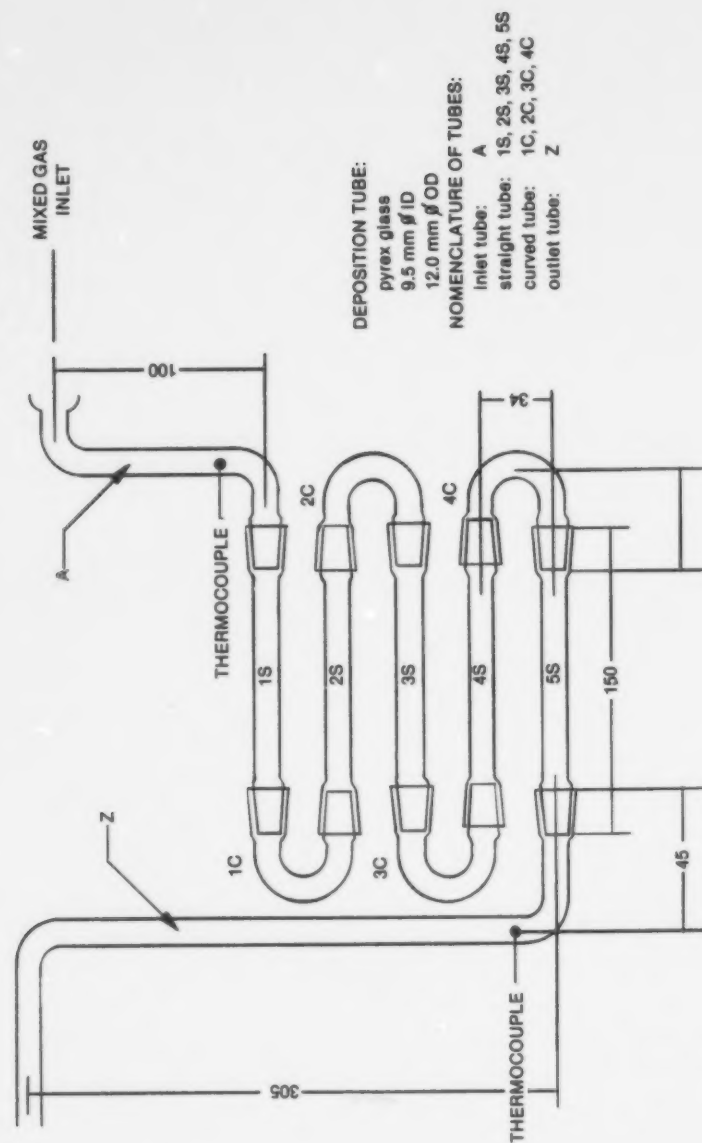


Figure 3-50 Tube Used for Ammonium Bisulfate Deposition Test.

70A2744

diameter and 1.2 m long. At the end of the test cycle these tubes are submerged in an oil bath kept at different temperatures ranging from 120 to 280°C. After the gas has passed through them for a certain period of time, the tubes are analysed for deposits.

Figure 3-51 shows the deposit ratio of  $\text{SO}_2$  and  $\text{NH}_3$  when a gas containing 200 ppm each of  $\text{SO}_2$  and  $\text{NH}_3$  with 10 percent  $\text{H}_2\text{O}$  was sent through the apparatus. A maximum deposit ratio (nearly 100 percent) was obtained at a temperature of 200°C and a velocity of 10 m/sec. It appears that the high gas velocity caused gas turbulence which in turn promoted deposit formation. The deposits were mainly  $\text{NH}_4\text{HSO}_4$  with a small amount of  $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$ ; the  $\text{NH}_3/\text{SO}_2$  mole ratio was almost 1.1.

Measurement of the deposits formed in each section of the tube at a gas velocity of 6 m/sec revealed that nearly all of the deposits formed within 60 cm of the inlet. This indicates that most of the deposits formed within 0.1 second after being introduced into the glass tube at 120–240°C.

Figure 3-52 shows the  $\text{NH}_3/\text{SO}_2$  mole ratios of the deposits formed in each section of the tube when gases with different mole ratios were passed through the tube at a temperature of 160°C. Despite differing inlet gas compositions the deposits formed at the inlet of the tube had ratios of about 1.1; the ratios of deposits formed downstream were closer to that of the inlet gas. Figure 3-53 indicates that the deposit ratio was the highest when the  $\text{NH}_3/\text{SO}_2$  mole ratio of the gas was around 1.1. The low melting point at the 1:1 ratio (Figure 3-46) may favor deposit formation. Figure 3-54 shows that the deposit ratio was nearly 100%, even with low  $\text{NH}_3$  and  $\text{SO}_2$  (10 ppm each) concentrations in the gas, although the tests using these low concentrations may contain experimental errors.

The tests described above show that deposits form very rapidly when the gas is cooled to the critical temperature, and that the deposit ratio of  $\text{SO}_2$  is usually slightly smaller than that of  $\text{NH}_3$ . A portion of the  $\text{SO}_2$  may form fine mists of  $\text{H}_2\text{SO}_4$  which have a tendency to pass through the tube along with



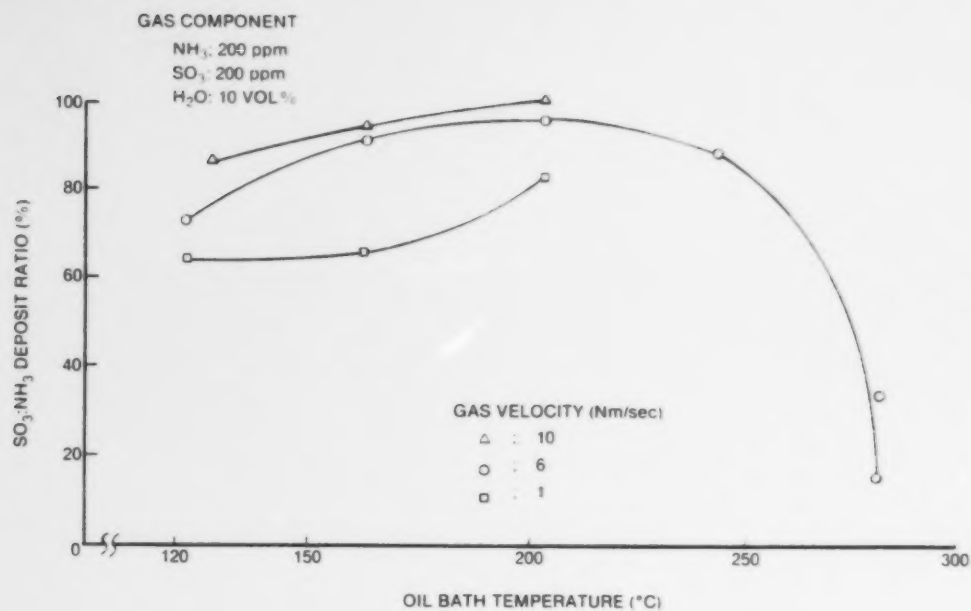


Figure 3-51 Gas Velocity and Deposition Ratio.

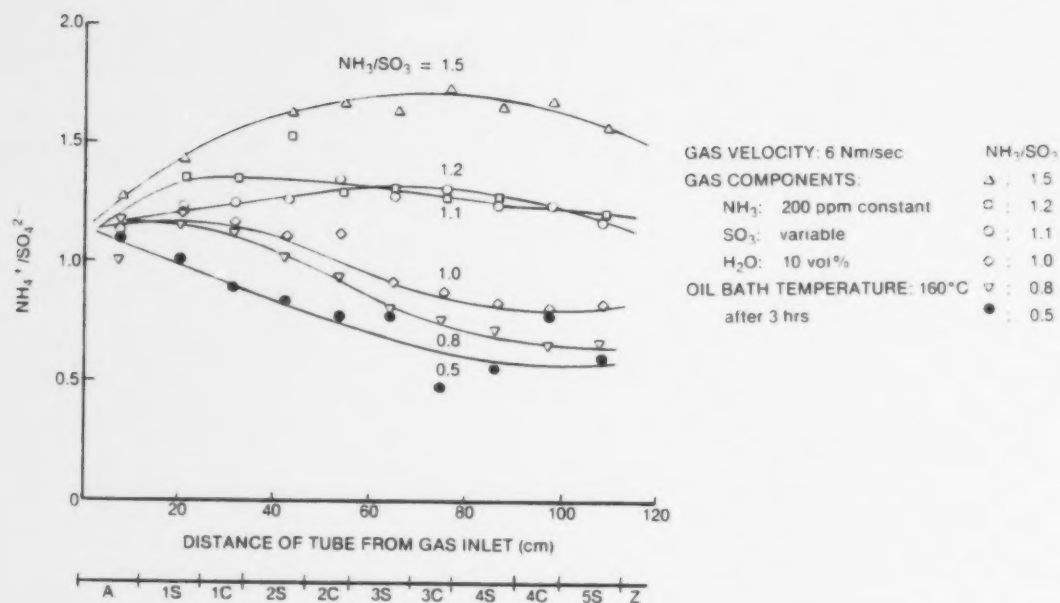


Figure 3-52  $\text{NH}_4/\text{SO}_4$  Ratio of Deposits Formed from Gases of Varying Compositions in Different Tube Sections.

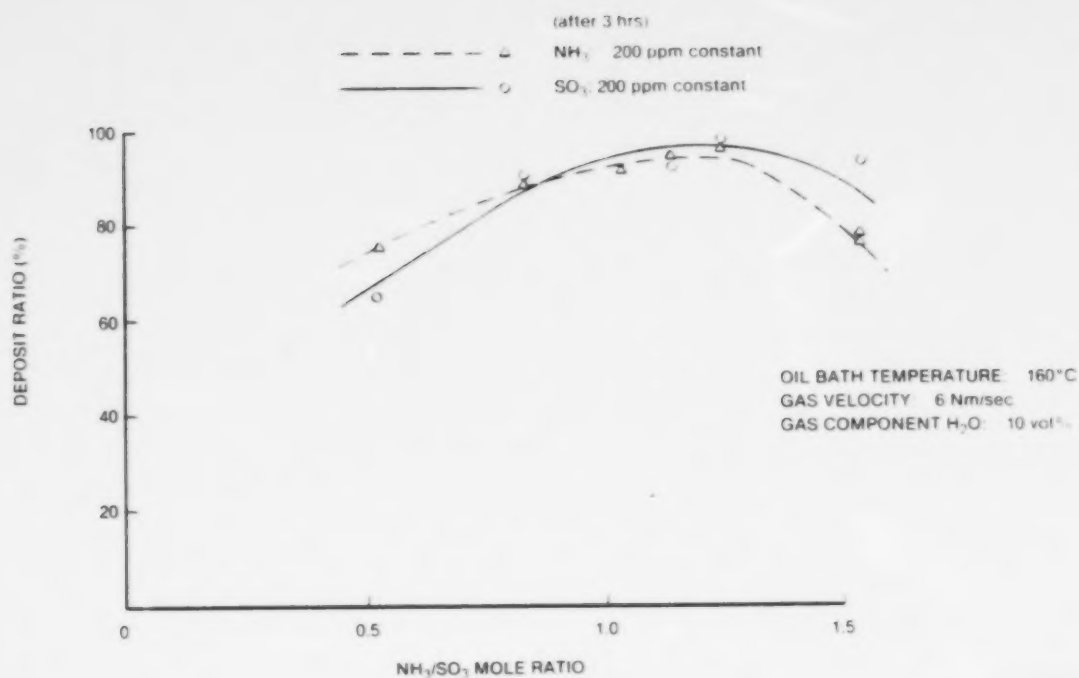


Figure 3-53  $\text{NH}_3/\text{SO}_3$  Mole Ratio vs. Deposit Ratio.

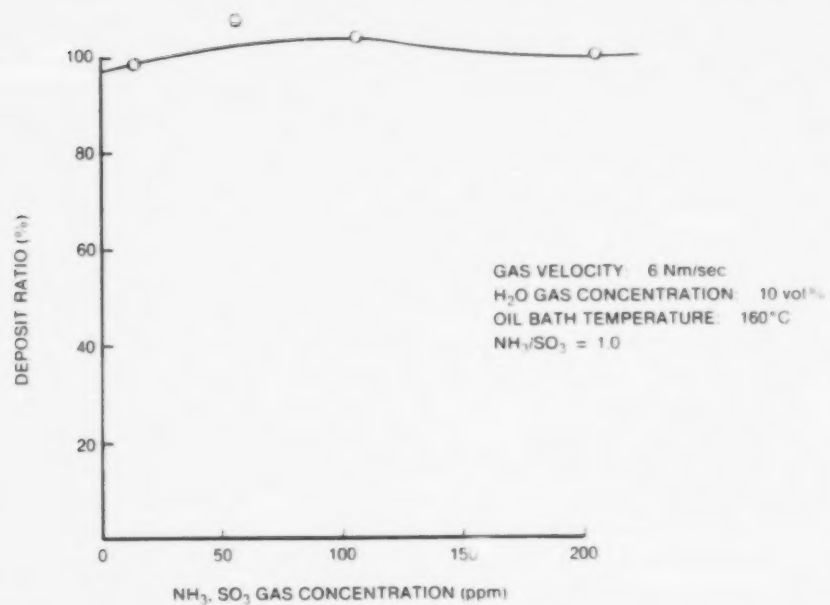


Figure 3-54 Inlet  $\text{SO}_3$  and  $\text{NH}_3$  Concentration vs. Deposit Ratio.

the gas. The  $\text{NH}_3$  in the gas is immediately absorbed by the deposits, particularly by those in the liquid phase.

Because the deposits are very hygroscopic, a considerable amount of liquid may be present even at temperatures between the melting point and  $100^\circ\text{C}$ . The liquid phase may be the most corrosive.

#### 3.6.4 Air Preheaters (Heat Exchangers)

There are two types of air preheaters or heat exchangers used to heat flue gases. These are shown in Table 3-16.

TABLE 3-16. TYPES OF AIR PREHEATERS (HEAT EXCHANGERS)

- 
- |                                        |
|----------------------------------------|
| 1. Rotating                            |
| a. Ljungstrom (with rotating elements) |
| b. Rothemuehle (with rotating hoods)   |
| 2. Multi-tube (no moving parts)        |
- 

Rotating preheaters have a better heat transfer efficiency and have been used mainly for treating a large amount of gas while multi-tube preheaters are simpler and have been used mainly for smaller gas sources.

For large boilers, Ljungstrom preheaters have been widely used. This type of preheater has rotating elements as shown in Figure 3-55. Flue gas leaves the boiler economizer (or SCR reactor) at  $300\text{--}400^\circ\text{C}$  and then passes through one side of the elements and is cooled to  $150\text{--}160^\circ\text{C}$ , while air or cold gas passes through the other side of the elements and is heated to  $250\text{--}300^\circ\text{C}$ . Figure 3-56 shows the temperatures of the gas, air, and heating elements. These temperatures usually fall into three zones: high-, intermediate-, and low-temperature. The temperatures of the elements are between those of the gas and air and fluctuate within a certain range as the elements rotate between the gas and air. For example, Figure 3-56 shows that at the boundary of the intermediate- and low-temperature zones, the temperatures of the gas and

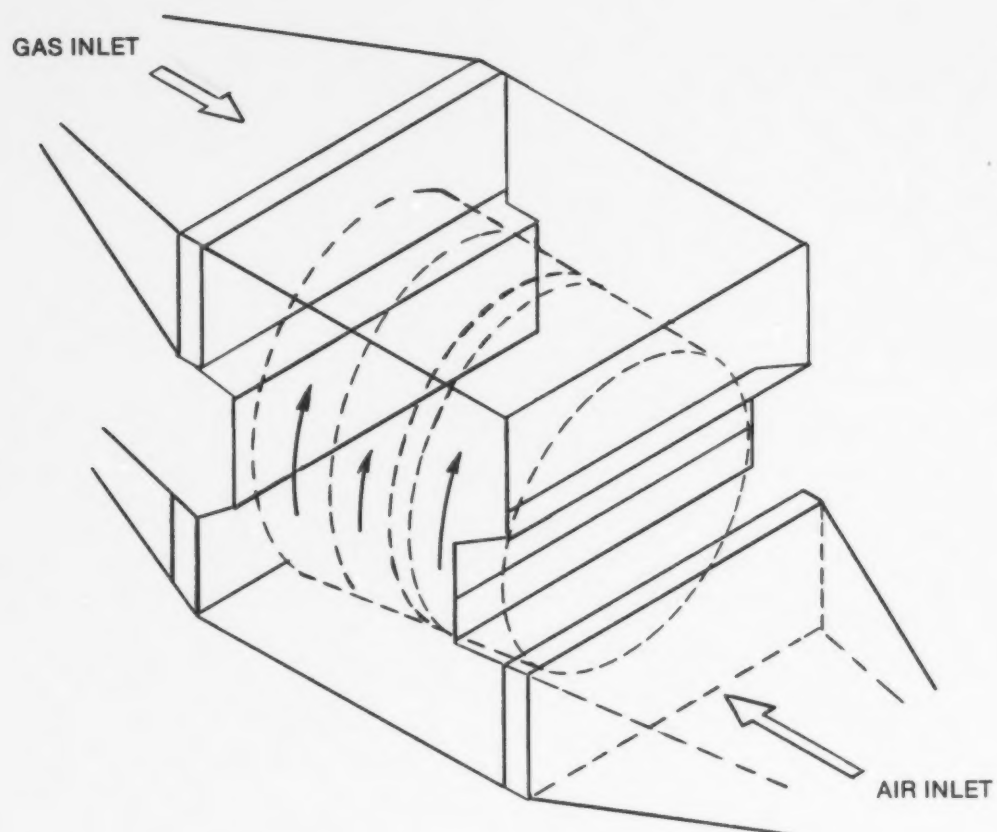


Figure 3-55 Schematic of Ljungstrom Air Preheater.

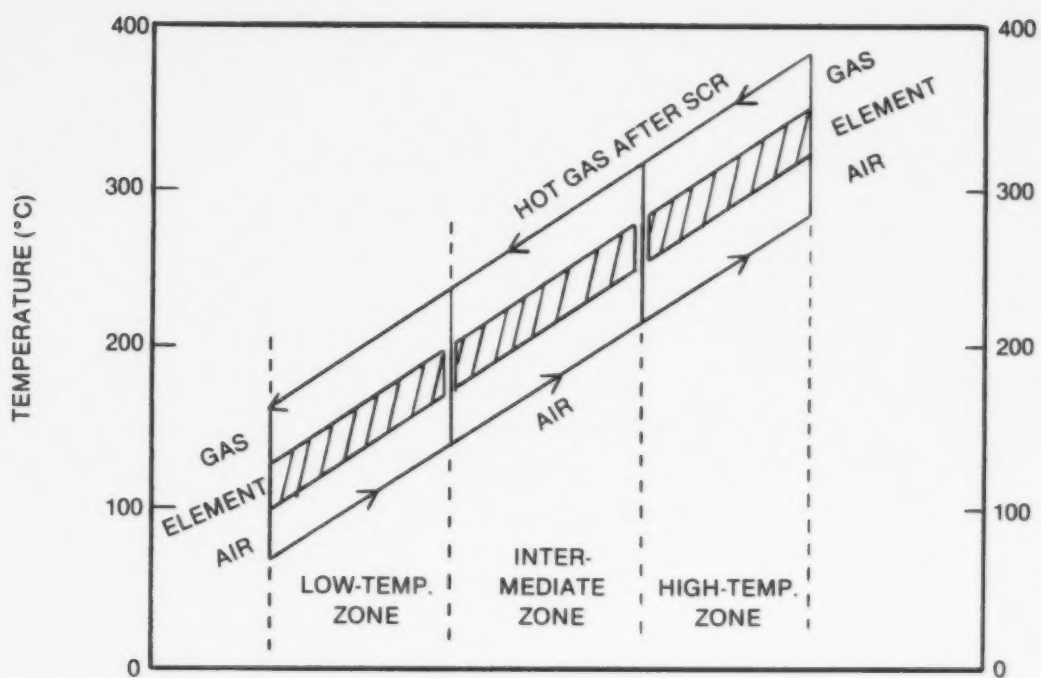


**Figure 3-56** Temperatures of Gas, Air and Heating Element in a Ljungstrom Air Preheater.

air are 230°C and 140°C respectively. At the same time the temperature of the elements fluctuates between 200 and 170°C. These are the most favorable temperatures for the formation of deposits.

The gas velocity through the heating elements is normally about 3 m/sec. The retention time for the gas in the preheater is approximately 1 second at a temperature below 230°C. During this time most of the SO<sub>2</sub> or NH<sub>3</sub> in the gas (whichever is present in a lower concentration) may precipitate to form ammonium bisulfate and related compounds while the rest of the SO<sub>2</sub> and NH<sub>3</sub> is released from the preheater.

An air preheater or heat exchanger usually has a soot blowing system on the cold side of the elements (Figure 3-57A). However, this system cannot effectively remove the deposits, particularly those formed between the elements in low-temperature and intermediate zones (Figure 3-57).

Recently an improved type of air preheater (Figure 3-57,B) has been used commercially. This preheater has two elements, with hot- and intermediate-, and low-temperature zones and a soot blowing system applied to both the cold and hot sides of the heater. This preheater is considerably more costly than conventional preheaters and is used with the low-dust SCR system to treat flue gas from coal. (Section 3.5.1)

Figure 3-58 shows two of the most popular kinds of heating elements. Tests have proven that the notched-flat type (Figure 3-58, A and Figure 3-44) is easier to clean with soot blowing than the notched-undulated type (Figure 3-60,B). Further studies are being conducted to develop heating elements which minimize the bisulfate problem.

Another rotating air preheater, the Rothemuehle type, is shown in Figure 3-59. It has stationary elements with a rotating hood for hot gas. Ammonium bisulfate deposits form in this preheater in the same way that they form in a Ljungstrom preheater.



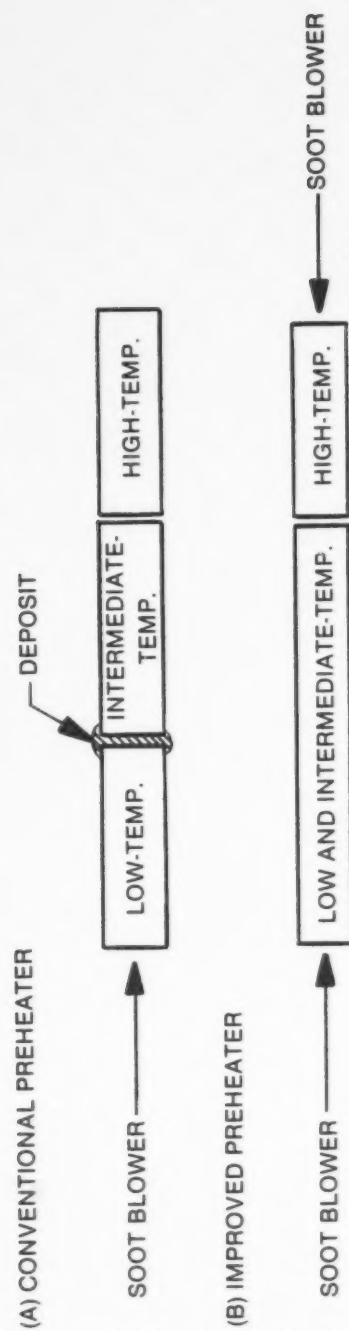


Figure 3-57 Heating Element Configurations in Conventional and Modified Ljungstrom Air Preheaters.

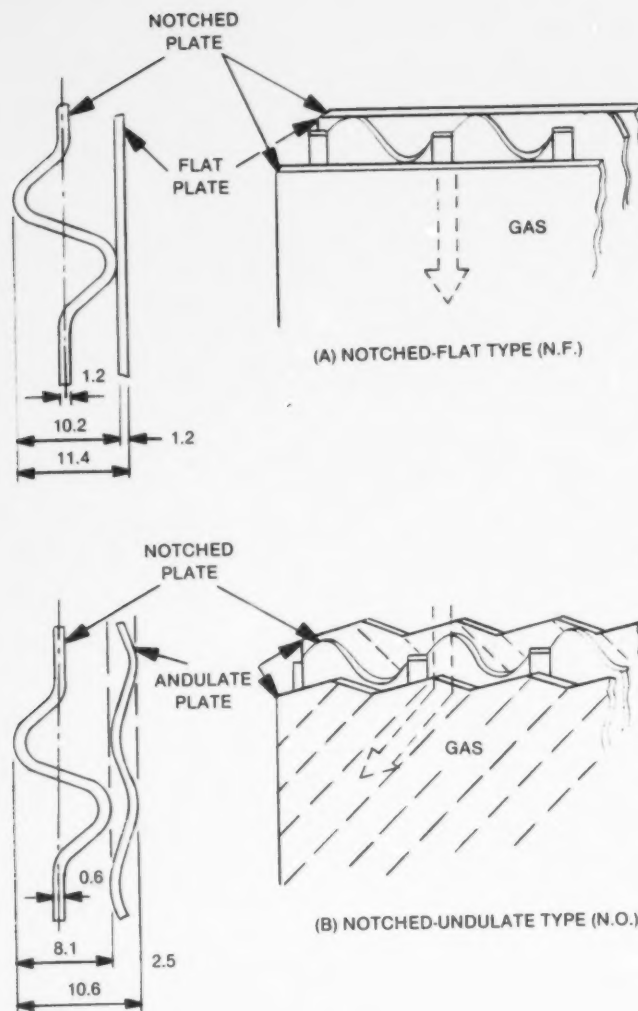


Figure 3-58 Two Types of Heating Elements.

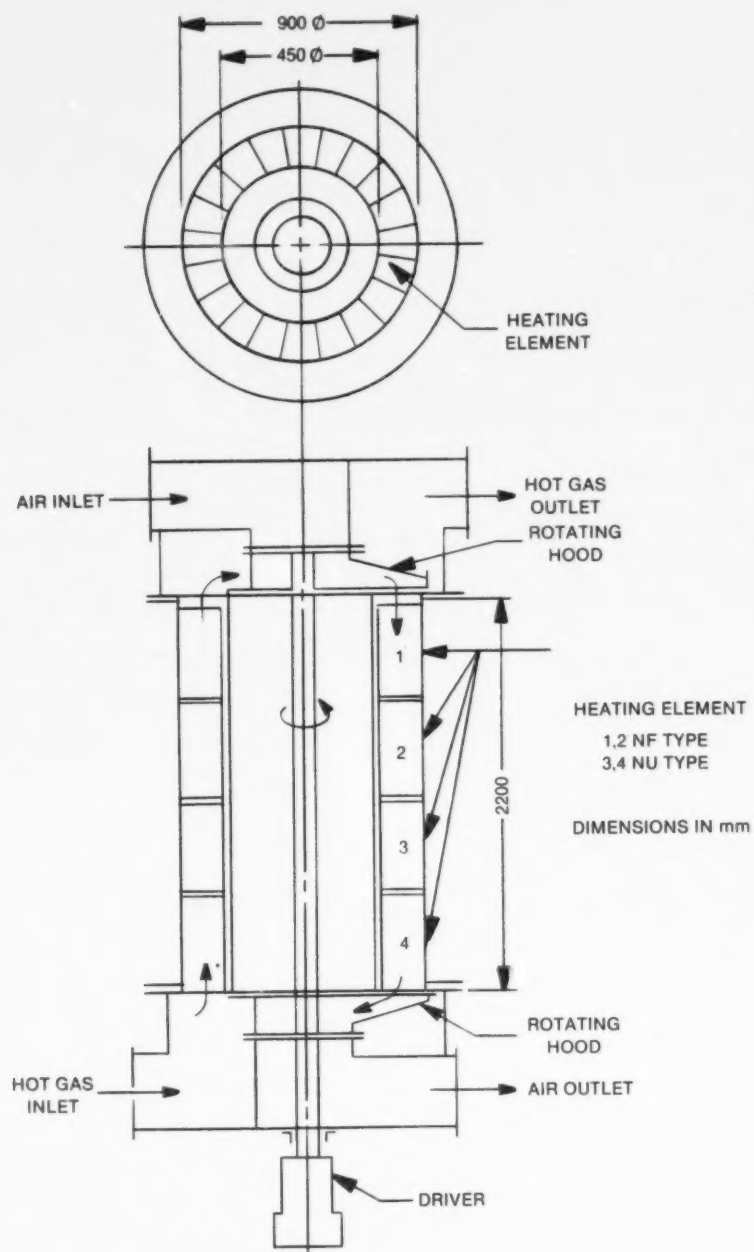


Figure 3-59 Rothemuehle Air Preheater Used in a Pilot Test Plant.

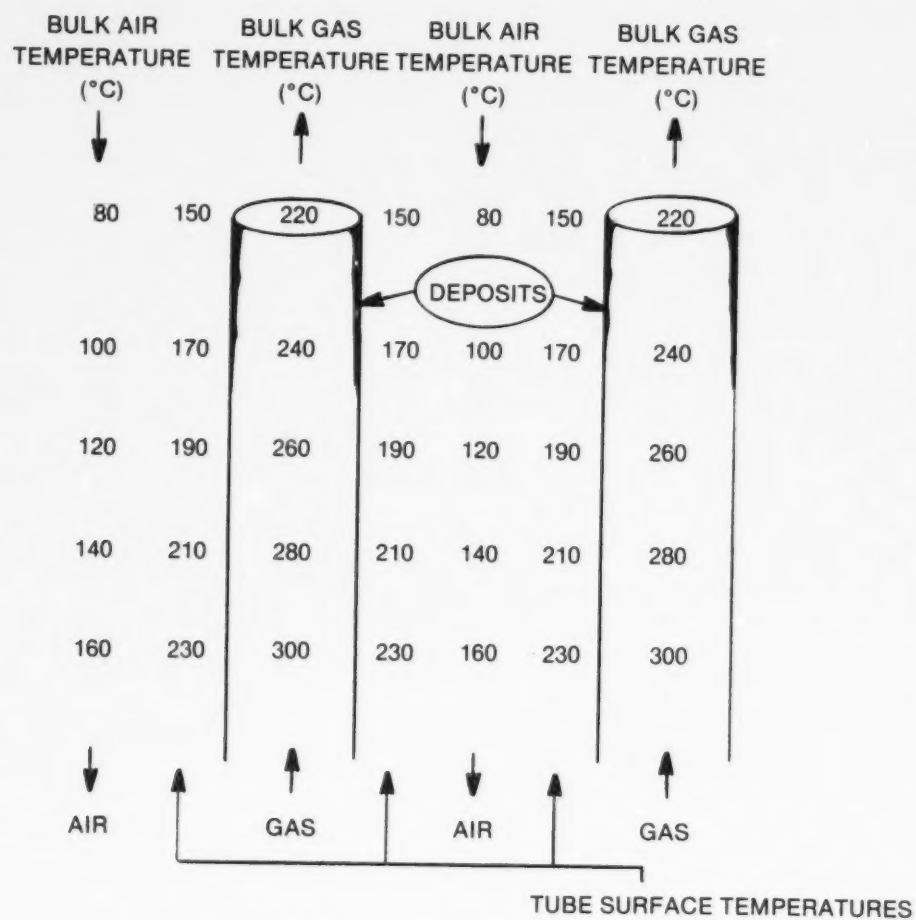


Figure 3-60 Deposits in Air Preheater Tubes.

Figure 3-60 shows the temperatures of the gas, air, and tubes as well as the deposits formed in a typical multi-tube air preheater. The preheater has been used with a 10 MW equivalent oil-fired industrial boiler with an SCR system. The 350°C gas leaves the SCR reactor and passes through the tubes with a velocity of 10 m/sec. The gas is then cooled to 220°C while air preheated to 80°C is passed outside the tubes and heated to 160°C. The deposits which formed inside the tube at temperatures below 200°C, were found to be the reaction product of ammonium bisulfate and the tube material.

### 3.6.5 Laboratory Corrosion Tests (15)

Corrosion tests have been conducted using four different steel samples. The chemical composition of the steels are shown in Table 3-17. Each sample was dipped into melted ammonium bisulfate at 200°C. As shown in Figure 3-61, low-alloy steel and SS 41 steel corroded slowly at the beginning and then fairly rapidly while stainless steels corroded rapidly at the onset and then more slowly after that. The corrosion rates of the stainless steels and aluminum are shown in Figure 3-62. The figure indicates that aluminum underwent little corrosion because it formed a protective coating.

Figures 3-63 and 3-64 illustrate that addition of ammonium sulfate reduces corrosion; the strong acidity of the bisulfate is weakened by the sulfate. On the other hand, corrosion is substantially increased by the addition of sulfuric acid as shown in Figure 3-65. Most of the liquid in the tube reacted with the steel in about 60 hours and the corrosion (as shown by the dotted line) almost stopped after that. The broken line of the figure shows the maximum amount of corrosion possible when a sufficient amount of the liquid is present.

Figure 3-66 shows that potassium chloride (KCl) promotes the corrosion process. The effects of various additives on corrosion are shown in Table 3-18. CaO, MgO, and Fe<sub>2</sub>O<sub>3</sub> reduced the corrosion because they neutralized the acidity of the liquid. Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> had little effect. Corrosion was increased substantially by NH<sub>4</sub>Cl, KCl, and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. This was due presumably to the following reactions:

TABLE 3-17. CHEMICAL COMPOSITION OF STEELS (%)

|                     | C    | Si   | Mn   | P     | S     | Cr    | Ni    | Cu   | Mo   |
|---------------------|------|------|------|-------|-------|-------|-------|------|------|
| SS 41 Mild Steel    | —    | —    | —    | <0.05 | <0.05 | —     | —     | —    | —    |
| Low-Alloy Steel     | 0.07 | 0.27 | 0.36 | 0.075 | 0.017 | 0.36  | 0.10  | 0.28 | —    |
| 304 Stainless Steel | 0.05 | 0.60 | 0.92 | 0.026 | 0.005 | 18.32 | 9.15  | —    | —    |
| 316 Stainless Steel | 0.06 | 0.59 | 1.06 | 0.031 | 0.004 | 16.90 | 12.50 | 0.29 | 2.29 |

TABLE 3-18. EFFECT OF ADDITIVES ON CORROSION OF LOW-ALLOY STEEL BY AMMONIUM BISULFATE AT 200° FOR 75 HOURS.

| Additive                              | None  | CaO   | MgO  | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | KCl   | NH <sub>4</sub> Cl | Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> |
|---------------------------------------|-------|-------|------|--------------------------------|--------------------------------|------------------|-------|--------------------|-------------------------------------------------|
| Amount of Additive (%)                | 0     | 18.3  | 20.0 | 16.7                           | 20.6                           | 37.5             | 25.9  | 27.5               | 27.0                                            |
| Corrosion rate (g/m <sup>2</sup> )    | 22.50 | 15.48 | 7.68 | 24.37                          | 14.39                          | 27.64            | 254.8 | 58.72              | 344.7                                           |
|                                       |       | 11.87 | 6.36 | 19.90                          | 10.44                          | 26.83            | 267.6 | 170.8              | 421.2                                           |
| Corrosion rate (g/m <sup>2</sup> /hr) | 0.30  | 0.21  | 0.10 | 0.32                           | 0.19                           | 0.37             | 3.40  | 0.78               | 4.60                                            |
|                                       |       | 0.16  | 0.08 | 0.27                           | 0.14                           | 0.36             | 3.53  | 2.28               | 5.62                                            |



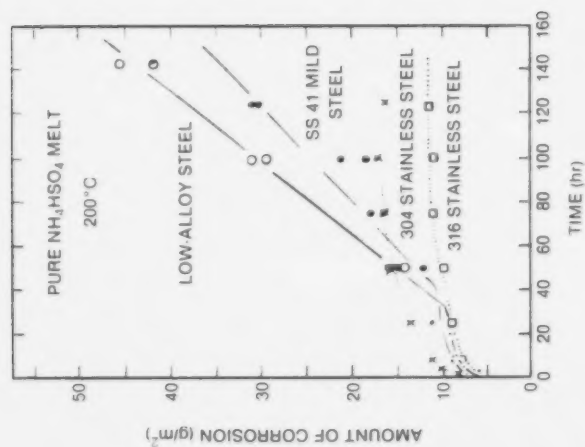


Figure 3-61 Corrosion of Steel by Ammonium Bisulfate.

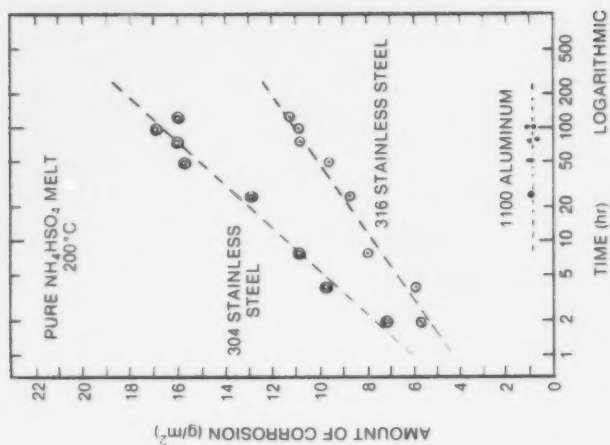


Figure 3-62 Ammonium Bisulfate Corrosion Rate of Stainless Steel and Aluminium.

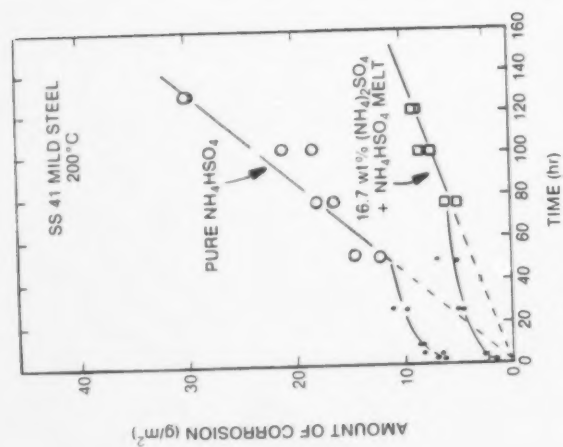


Figure 3-63 Corrosion of Mild Steel by Ammonium Bisulfate Showing the Effect of Ammonium Sulfate.

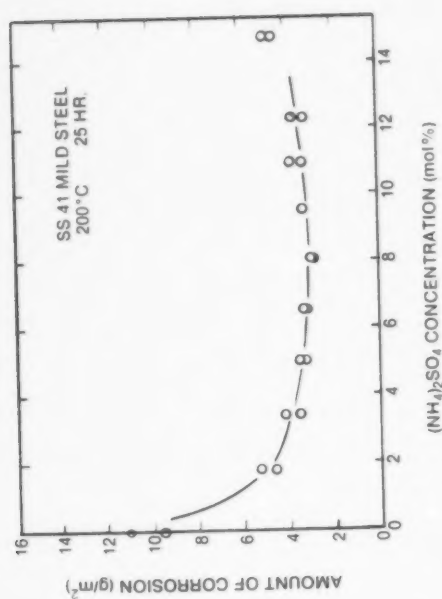


Figure 3-64 Effect of  $(\text{NH}_4)_2\text{SO}_4$  on Corrosion of Mild Steel by Ammonium Bisulfate.

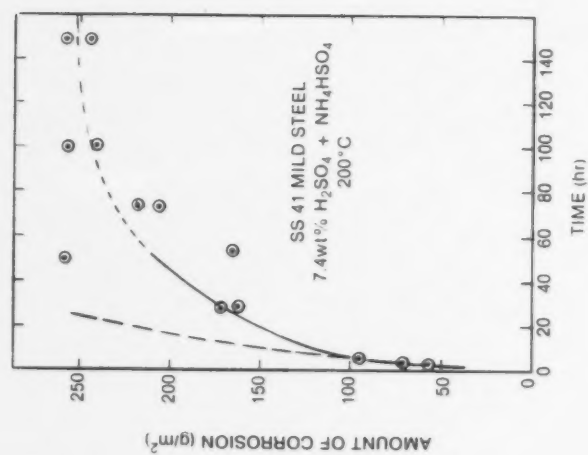


Figure 3-65 Corrosion of Mild Steel by Sulfuric Acid. Containing Ammonium Bisulfate.

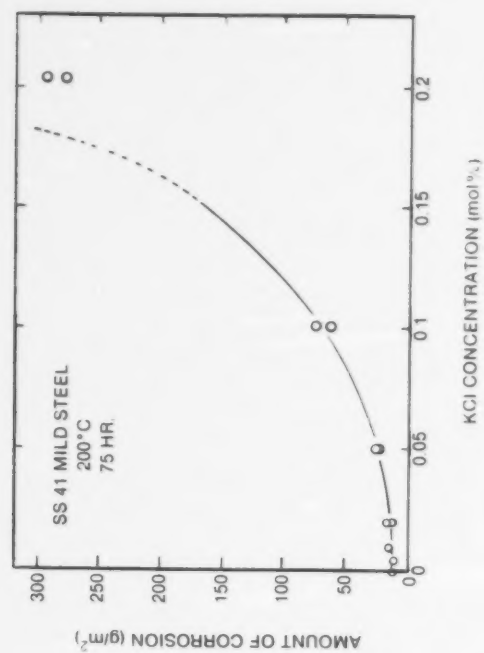
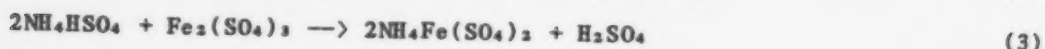
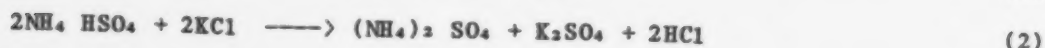
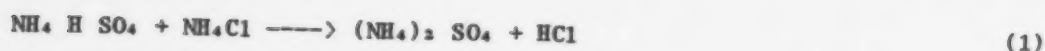
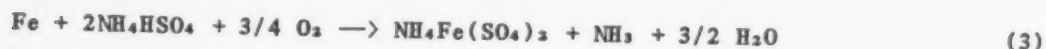
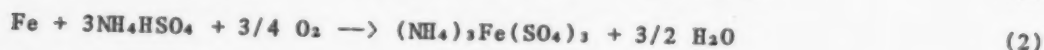
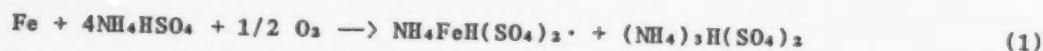


Figure 3-66 Effect of Potassium Chloride on Corrosion of Mild Steel by Ammonium Bisulfate.



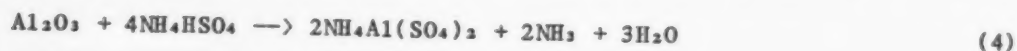
### 3.6.6 Ammonium Bisulfate/Iron and Fly Ash Reaction Products (16)

The author has studied the reactions of ammonium bisulfate with iron and fly ash at temperatures ranging from 150° - 300°C. When ammonium bisulfate reacted with iron the major products were  $\text{NH}_4\text{FeH}(\text{SO}_4) \cdot \text{H}_2\text{O}$ ,  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ ,  $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$ , and  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ . These products indicate that the following reactions occurred:



The first reaction (1) occurred readily at the low temperatures (150°-200°) while the third reaction (3) occurred readily at the higher temperatures of 250°C or above. The intermediate temperatures promoted the second reaction (2).

Upon heating, the aluminum and calcium in the fly ash reacted with ammonium bisulfate to form  $\text{NH}_4\text{Al}(\text{SO}_4)_2$  and  $\text{CaSO}_4$  by the following reactions:



These reaction products are the major compounds which comprise the deposits found in air preheaters and heat exchangers.

### 3.6.7 Compounds in Air Preheater and Heat Exchanger Deposits (13,16)

This author also used X-ray diffraction to determine the composition of

the deposits found in a heat exchanger and two air preheaters. Table 3-19 lists the samples. Two of the deposit samples (A-1 and A-2) were obtained from a commercial heat exchanger for flue gas from an oil-fired industrial boiler. In this system the 60°C gas leaves the FGD system while the hot gas leaves the SCR reactor at 400°C. Samples B-1 and B-2 were obtained from an air preheater at a SCR pilot plant which treats coal-fired boiler flue gas. Samples C-1 and C-7 were obtained from seven different temperature zones of a commercial air preheater. The preheater was used with a flue gas from an oil-fired utility boiler (low-sulfur oil) subjected to SNR (Thermal DeNO<sub>x</sub>).

The results of the analysis of these samples are shown in Table 3-20. Samples A-1 and A-2 were composed of  $\text{NH}_4\text{FeH}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ . This compound is formed by reaction (1) described in Section 3.6.6. A-1 also contained  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  which did not form by the reaction of  $\text{NH}_4\text{HSO}_4$  and Fe. This indicates that sulfuric acid condensed and reacted with Fe to form the compound; the flue gas is rich in  $\text{SO}_3$  and lean in  $\text{NH}_3$ . Samples B-1 and B-2 contained  $\text{NH}_4\text{Al}(\text{SO}_4)_2$  and  $\text{CaSO}_4$  in addition to fly ash and  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ . The aluminum and calcium compounds were formed by the reaction of  $\text{NH}_4\text{HSO}_4$  with fly ash from coal (Section 3.6.6).

Sample deposits C-1 through C-7 formed in a gas which was rich in  $\text{NH}_3$  and lean in  $\text{SO}_3$ .  $(\text{NH}_4)_2\text{SO}_4$  was present in the deposits in the low-temperature zones (C-1 through C-3), while  $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$  was present in the deposits in the intermediate zones (C-2 through C-4). Reaction products of  $\text{NH}_4\text{HSO}_4$  with Fe were present in C-4 through C-7, indicating that corrosion occurred in the high temperature zones. All of the deposits contained a large amount of unburned carbon, which indicated that carbon seemed to increase the amount of deposition and promoted plugging.

Tests on the three sets of samples also revealed that almost no  $\text{NH}_4\text{HSO}_4$  was present in the deposits.  $\text{NH}_4\text{HSO}_4$  is very corrosive and had reacted with Fe and fly ash to form various compounds.

TABLE 3-19. DEPOSITS AND GAS COMPOSITIONS

| System | Sample No. | Location                                              | Boiler Fuel           | SO <sub>2</sub> (ppm) | NH <sub>3</sub> (ppm) |
|--------|------------|-------------------------------------------------------|-----------------------|-----------------------|-----------------------|
| A      | A-1, A-2   | Shindaikoywa<br>Petrochemical's<br>Yokkaichi<br>Plant | High-Sulfur<br>Oil    | 30-40                 | 10                    |
| B      | B-1, B-2   | EPDC's Test<br>Facility                               | Medium-Sulfur<br>Coal | 3-15                  | 10-20                 |
| C      | C-1 - C-7  | Chuba Electric's<br>Chita Plant                       | Low-Sulfur<br>Oil     | 2-3                   | 20-30                 |

### 3.6.8 Deposit Formation Reduction

Ammonium bisulfate deposition may be reduced in 5 main ways: 1) reduction of unreacted NH<sub>3</sub>; 2) reduction of SO<sub>2</sub>; 3) combustion control to reduce soot in oil-fired burners; 4) use of coal fly ash for cleansing; and 5) selection of appropriate air preheater elements/soot blowing systems. Reducing unreacted NH<sub>3</sub> is the most commonly used method of decreasing bisulfate formation. This can be accomplished by lowering the inlet NH<sub>3</sub>/NO<sub>x</sub> mole ratio to less than 1.0 and simultaneously using a large amount of catalyst. Keeping unreacted NH<sub>3</sub> below 5 ppm will substantially reduce deposition but may not solve the problem entirely. Some of the SCR plants maintain an unreacted NH<sub>3</sub> concentration of less than 2 ppm to minimize deposit formation. (Sections 4.4 and 5.2). On the other hand, with a low unreacted NH<sub>3</sub> concentration, acidic deposits with NH<sub>3</sub>/SO<sub>2</sub> mole ratios below 1.0 may form, causing corrosion.

SO<sub>2</sub> can be reduced in 3 ways: 1) by using low-sulfur fuel; 2) by combustion control in order to use a minimum amount of excess air; and 3) by using a low-oxidation SCR catalyst. When the gas is lean in SO<sub>2</sub> and rich in NH<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>H(SO<sub>4</sub>)<sub>2</sub> will be formed at higher temperatures and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> will form at lower temperatures. Both of these compounds are less corrosive than NH<sub>4</sub>HSO<sub>4</sub>. The deposits may be removed quite easily with the soot blower.



For oil-fired boilers, combustion control to reduce soot (unburned carbon) is a good way to decrease deposits. Soot tends to form deposits along with the  $\text{NH}_3$  and  $\text{SO}_3$  compounds, thereby causing an increase in plugging. The cleansing effect of coal fly ash can be observed in a boiler burning pulverized coal with a full dust load. At an adequate gas velocity there will be little or no bisulfate problem primarily because the bisulfate deposits on the ash. In this case, however, the unreacted  $\text{NH}_3$  concentration in the flue gas must be kept low in order to reduce the contamination of the ash by the ammonium compounds. Selecting the appropriate air preheater elements and using an effective soot blowing system also will minimize ammonium bisulfate deposition. If these measures are used, the air preheater may be operated continuously for over a year without bisulfate problems.

However, considerable deposition may still occur in some of the SCR plants which use high sulfur oil or a low-dust system for coal. The deposits usually do not hinder the heat transfer efficiency to any great extent, but do increase the pressure drop of the gas in the preheater. When the pressure drop exceeds a certain level, it is necessary to interrupt the operation of the preheater for a water wash. Usually about one day is needed for the wash, which includes the cooling of the preheater, water washing, and drying. Since the wash water becomes acidic when it mixes with the bisulfate and related compounds (Table 3-20), wastewater treatment may be needed for neutralization and also to remove ammonia.

Recently, Chugoku Electric developed a new method of removing deposits called thermal cleaning which may be superior to water washing. (Section 4.3.4).

### 3.7 OTHER PROBLEMS WITH AMMONIA

#### 3.7.1 Introduction

In addition to the bisulfate problem described in the previous section, ammonia also has the following effects on flue gas treatment systems:

TABLE 3-20. COMPOUNDS IN DEPOSITS IN HEAT EXCHANGER AND AIR PREHEATER (16)

| Sample Number | Temperature Zone         | Estimated temp. (°C) | Major                                                           | Medium                                    | Minor                                                | pH <sup>b</sup> |
|---------------|--------------------------|----------------------|-----------------------------------------------------------------|-------------------------------------------|------------------------------------------------------|-----------------|
| A-1           | Low (cold)               | 90-110               | $\text{NH}_4\text{FeH}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ | $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  | $\text{NH}_4\text{HSO}_4$                            | 1               |
| A-2           | Low (Int. <sup>a</sup> ) | 110-130              | $\text{NH}_4\text{FeH}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ | $\text{NH}_4\text{Fe}(\text{SO}_4)_2$     | $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$            | 1               |
| B-1           | Int.                     | About 200            | Fly Ash                                                         | $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ | $\text{NH}_4\text{Al}(\text{SO}_4)_3, \text{CaSO}_4$ | 1               |
| B-2           | Int.                     | About 200            | Fly Ash                                                         | $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ | $\text{NH}_4\text{Al}(\text{SO}_4)_3, \text{CaSO}_4$ | 1               |
| C-1           | Low (cold)               | About 120            | Carbon                                                          | $(\text{NH}_4)_2\text{SO}_4$              |                                                      | 3               |
| C-2           | Low (hot)                | >120                 | Carbon                                                          | $(\text{NH}_4)_2\text{SO}_4$              | $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$             | 1               |
| C-3           | Int. (cold)              | About 160            | Carbon                                                          | $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ | $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$             | 1               |
| C-4           | Int. (Int.)              | >160                 | Carbon                                                          | $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ | $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$             | 1               |
| C-5           | Int. (hot)               | About 200            | Carbon                                                          | $\text{NH}_4\text{Fe}(\text{SO}_4)_2$     | $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$            | 1               |
| C-6           | High (cold)              | >200                 | Carbon                                                          | $\text{NH}_4\text{Fe}(\text{SO}_4)_2$     | $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$            | 1               |
| C-7           | High (hot)               | About 250            | Carbon                                                          | $\text{NH}_4\text{Fe}(\text{SO}_4)_2$     |                                                      | 1               |

<sup>a</sup> Intermediate<sup>b</sup> Measured roughly with 15 percent aqueous solution.

- (1) Dust removal improvement (with ESP's).
- (2) Ammonium bisulfate deposition on the catalyst.
- (3) Fly ash contamination.
- (4) Plume formation.
- (5) Effects on FGD system.

### 3.7.2 Dust Removal Improvement

In Japan, ammonia injection is often used to improve ESP dust removal. Ammonia is injected into oil-fired utility boiler flue gas as it leaves the air preheater. This is done in order to improve the soot removal efficiency of the ESP and to prevent corrosion of the ESP by sulfuric acid mists in the gas.

For flue gas from coal, the dust removal efficiency may be increased by using a small amount of ammonia--up to 50 ppm for high sulfur coal, 20 ppm for low sulfur coal. Larger amounts of ammonia may cause excessive adhesion of fly ash to ESP collector plates (17). With baghouses, ammonia leakage from SCR systems could potentially require more frequent cleaning and bag replacement (17). These effects, however, have not really been demonstrated in Japan because of the low ammonia emissions, normally below 5 ppm.

### 3.7.3 Ammonium Bisulfate Deposition on SCR Catalysts

Ammonium bisulfate and related compounds tend to deposit on SCR catalysts even at temperatures above 300°C; they deposit in air preheaters at a temperature usually below 250°C. Deposition at the higher temperature may be caused by the high SO<sub>2</sub> concentration on the catalyst surface due to the oxidation of SO<sub>2</sub>, as well as to the high NH<sub>3</sub> concentration in the reactor. The critical temperature for deposition may be as high as 350°C with an SO<sub>x</sub>-rich gas and a high-oxidation catalyst.

The bisulfate essentially lowers catalytic activity by coating the catalyst surface and may even poison some types of catalysts. Most catalysts used for SO<sub>x</sub>-containing gases are not poisoned, however, and their activity can

be recovered when they are heated to 400-450°C and the bisulfate is volatilized. With low-temperature catalysts used at 200-250°C, deposit formation is a serious problem and necessitates occasional heating (Section 3.3).

In utility boilers, the economizer outlet gas temperature usually ranges from 350° - 400°C but may drop to 300-330°C when the boiler load is lowered at midnight, for example. A small amount of the bisulfate may deposit on the catalyst but is volatilized as the temperature increases with an increased load, thus causing no problem for SO<sub>x</sub>-lean gas. With SO<sub>x</sub>-rich gas, however, the NO<sub>x</sub> removal efficiency may be noticeably lowered when the gas temperature is kept below the critical temperature for several hours.

In order to maintain the temperature above the critical level, an economizer by-pass system has been used with some coal-fired utility boilers. Oil-firing has been used for the same purpose at smaller gas sources. A moving-bed reactor is used for treating a low-temperature gas of 200-250°C; the contaminated catalyst is removed from the reactor and heated.

#### 3.7.4 Contamination of Fly Ash by Ammonia

Ammonium bisulfate may deposit on fly ash in the gas stream (unreacted NH<sub>3</sub>) at temperatures below 250°C. Figure 3-67 shows the relationship between unreacted ammonia (NH<sub>3</sub> leakage) and the ammonia content of fly ash caught by a cold ESP downstream of an air preheater. The ammonia content increased almost linearly until it reached about 800 mg/kg at about 20 ppm of unreacted NH<sub>3</sub> in the gas. It did not increase significantly after that, presumably because of the limited SO<sub>3</sub> content of the gas which combines with NH<sub>3</sub> to form the deposits. Figure 3-67 indicates that the ammonia content of the ash was nearly 200 mg/kg (0.02%) with 5 ppm unreacted NH<sub>3</sub> and around 600 mg/kg with about 15 ppm unreacted NH<sub>3</sub>.

When used in concrete or landfill materials, an NH<sub>3</sub>-rich ash may produce an ammonia odor. This occurs when the alkaline component of the ash reacts with water. This reaction can be expressed as:

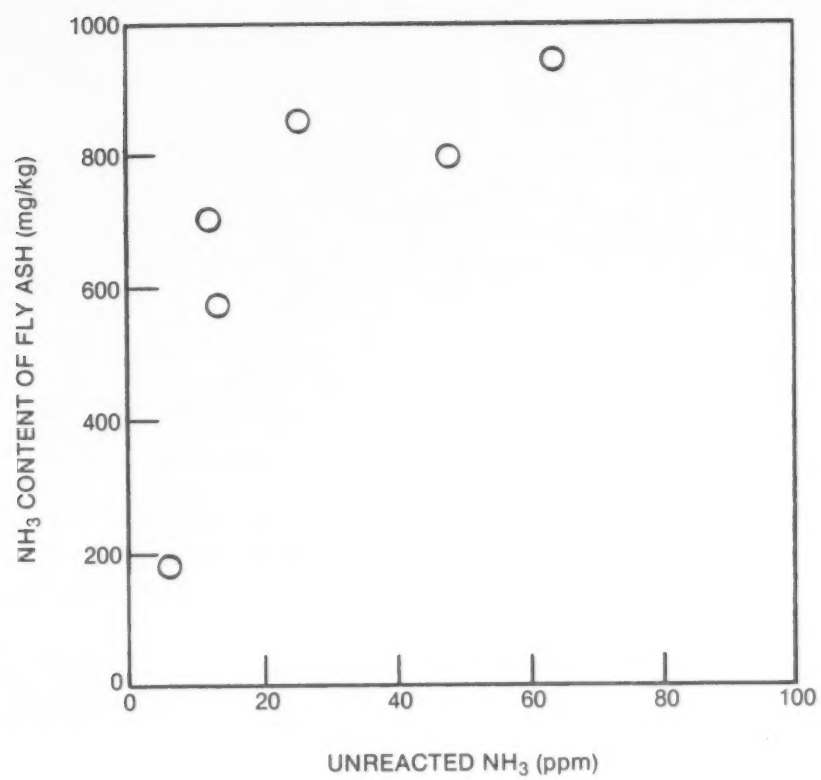
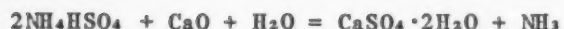


Figure 3-67 Adsorption of Unreacted NH<sub>3</sub> on Fly Ash. (6)



When  $\text{NH}_3$  is present in the ash, it also may cause water pollution problems. For these reasons it is best to maintain an acceptable level of  $\text{NH}_3$  in the ash. It has been found that an  $\text{NH}_3$  content below 0.02% works well. When SCR reactor outlet gas contains 5 ppm  $\text{NH}_3$  and 90% of the  $\text{NH}_3$  is caught by the ash present in 20 grams/ $\text{Nm}^3$  in flue gas (20 gm/ $\text{Nm}^3$ ) the  $\text{NH}_3$  content of the fly ash is 0.14%.

Chugoku Electric's Shimonoseki Power Station (Section 4.4) maintains unreacted  $\text{NH}_3$  below 2 ppm and has produced fly ash which can be used without problems for cement or concrete, or for landfill material.

If necessary,  $\text{NH}_3$  may be removed from the fly ash at the power plant by mixing it with a small amount of moisture. This causes reaction (1) to occur and release  $\text{NH}_3$ ; the released  $\text{NH}_3$  can be emitted from the stack without any trouble. Moistening the ash also can help prevent dust formation during ash handling.

### 3.7.5 Plume Formation

Plume problems caused by ammonia in flue gas have been known to occur when the gas from an ammonia-scrubbing FGD plant contains more than 10 ppm  $\text{NH}_3$ . On the other hand, there is no plume problem associated with flue gas which has undergone SCR. This is true even when the gas has been cooled to 140°C and contains 20 ppm  $\text{NH}_3$ . A plume has been observed during the winter with flue gas containing 50 ppm  $\text{NH}_3$  after selective noncatalytic reduction (thermal De- $\text{NO}_x$ ) (Section 6.2).

The difference in the plume formation associated with wet FGD and dry De- $\text{NO}_x$  systems is due to differences in moisture content and temperature as well as in the amount and particle size of ammonium compounds in the flue gases. With wet FGD, the 55°C moisture-saturated gas contains a large amount of  $\text{SO}_2$  and a considerable amount of  $\text{SO}_3$  before it is heated to 70-120°C. In the dry De $\text{NO}_x$  system, flue gas containing a smaller amount of moisture is



cooled from about 400°C to 150°C in an air preheater. In the preheater nearly all of the SO<sub>2</sub> combines with NH<sub>3</sub> to precipitate out as long as NH<sub>3</sub> is present in excess.

Plume problems may occur when flue gas containing a considerable amount of NH<sub>3</sub> after dry DeNO<sub>x</sub> is introduced into a wet FGD system. This is described in the following section.

### 3.7.6 Effect of Ammonia on Flue Gas Desulfurization

The effect of ammonia on flue gas desulfurization varies with the FGD system being used. Three types of wet process FGD systems popular in Japan are shown in Figure 3-68. No. 1 shows limestone scrubbing with a prescrubber in which over 90% of the ammonia in the gas is caught in the prescrubber by an acidic liquor with a pH of about 1. A typical FGD system for a 175 MW coal-fired boiler releases 5/hr of wastewater from the prescrubber. The ammonia content of the wastewater is calculated at roughly 200 ppm, assuming an inlet gas ammonia concentration of 3 ppm. The liquor is sent to a wastewater treatment system where ammonia may be removed either by a conventional activated sludge process or an ammonia stripping process, if necessary. Ammonia stripping has been applied at Chubu Electric's Owase Plant (18); the activated sludge process will be applied at the EPDC's Takehara Plant. The prescrubber outlet gas contains only a small amount of ammonia (below 1 ppm), most of which is caught by the scrubber but does not affect the scrubber system.

No. 2 shows a two-stage limestone scrubbing system. The first scrubber catches 60-70% of the ammonia in the flue gas while the second scrubber removes another 10-20% of the ammonia, which adds up to a total removal efficiency of 70-90%. The ammonia in the scrubber liquor may increase SO<sub>2</sub> removal efficiency and may not produce any adverse effects on the scrubber system (17). The by-product sludge, however, may cause environmental problems.

In Japan, sludge is oxidized to produce gypsum which is subsequently centrifuged and washed with water for use as cement, wallboard, and other

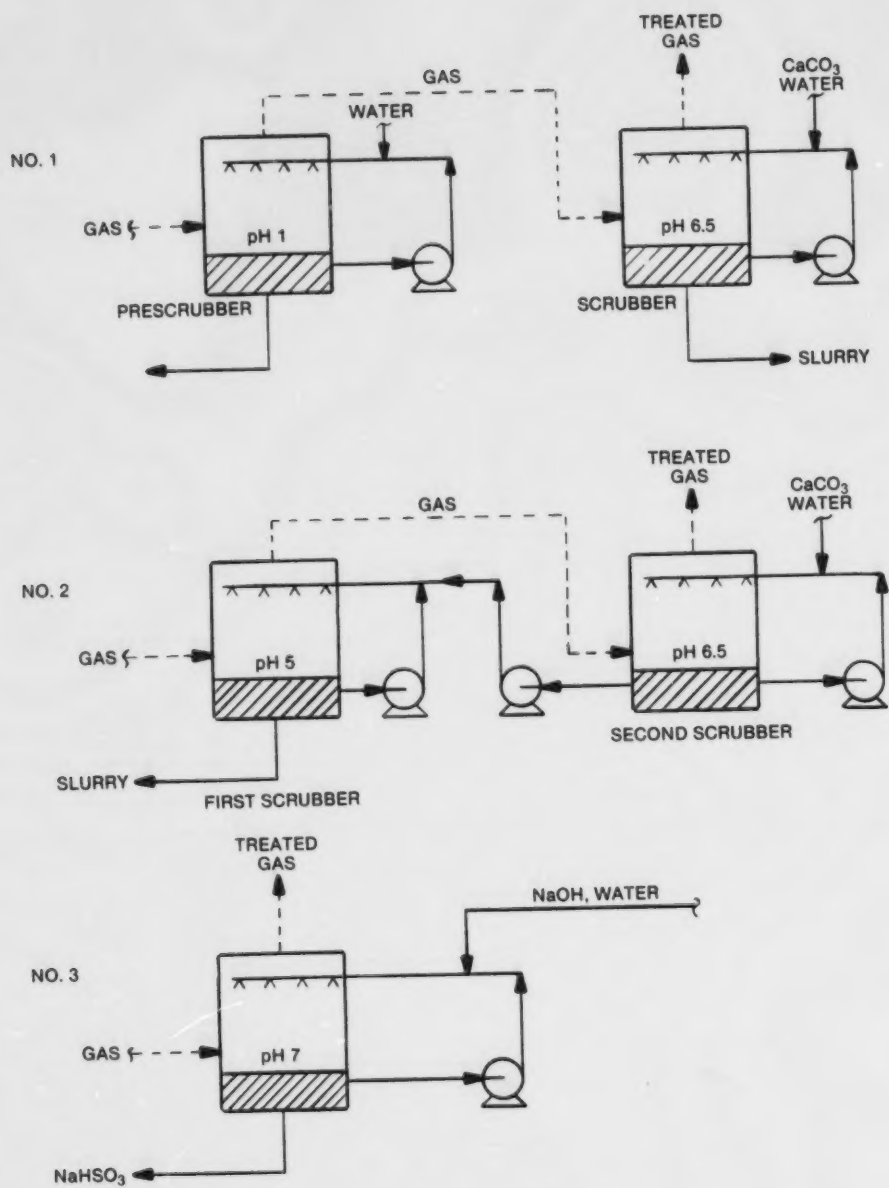


Figure 3-68 Three Most Popular Wet Process FGD Systems Used in Japan.

materials. Both the filtrate and the wash liquor are recycled in the scrubber system and a portion of the scrubber liquor is sent to the wastewater treatment system. If necessary, ammonia may be removed from the liquor to prevent environmental problems.

In FGD systems No. 1 and No. 2, flue gas leaving the scrubber contains little ammonia and will not cause a plume problem except in cases when inlet gas containing over 20 ppm  $\text{NH}_3$  enters System No. 2.

No. 3 shows simple sodium scrubbing which produces throw-away sodium sulfite or sulfate liquor. Approximately one-half of the  $\text{NH}_3$  in the flue gas is caught by the scrubber liquor. Removal of ammonia from the waste liquor may be necessary under certain circumstances. (A plume can be observed at the scrubber outlet of this system when the inlet flue gas contains more than about 20 ppm  $\text{NH}_3$ .)

### 3.7.7 Measurement of Ammonia in Flue Gas

The measurement of unreacted  $\text{NH}_3$  in flue gas is important both for control of  $\text{NO}_x$  removal efficiency and prevention of the problems described above. However, this measurement can be difficult for the following reasons:

- (1) Ammonia is usually present in a small concentration, below 10 ppm.
- (2) The presence of  $\text{NO}_x$ ,  $\text{SO}_x$ , etc. interferes with the measurement of ammonia.
- (3) At a large plant, the ammonia concentration may be different in each part of the large duct, causing sampling problems.

The major analytical methods used to measure  $\text{NH}_3$  in Japan are shown in Table 3-21 and Figure 3-69, I and II. Method I is used to measure the concentrations of  $\text{NO}_x$  and a total of  $\text{NO}_x$  and  $\text{NH}_3$ , after  $\text{NH}_3$  is converted to  $\text{NO}$ ; the  $\text{NH}_3$  concentration equals the difference between these two concentrations.



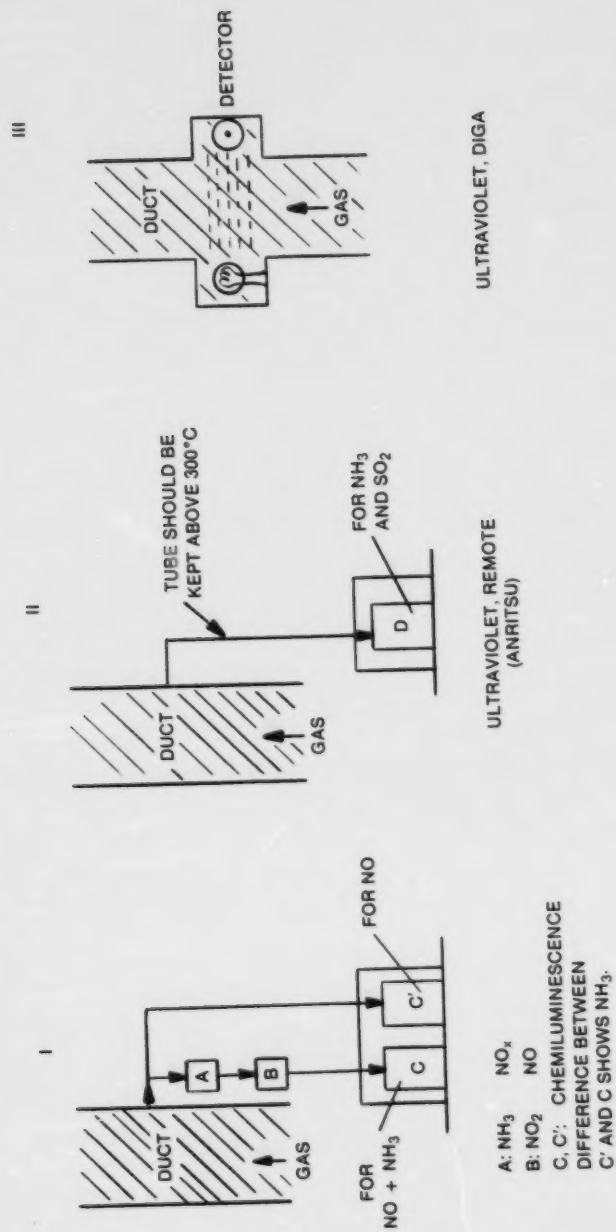


Figure 3-69 Comparison of NH<sub>3</sub> Analysis Methods.



With this method there may be a large analytical error when the  $\text{NO}_x$  concentration is much higher than the  $\text{NH}_3$  concentration, as is often the case with flue gases after SCR. A modified method for the determination of a low concentration of  $\text{NH}_3$  has been developed, and will be described in Section 4.4.3.

Method II is used for direct analysis of  $\text{NH}_3$ . However, any  $\text{SO}_x$  present in the gas interferes with the measurement, requiring a special calibration in order to take the interference into account. When using this method, the analytical error may be large if the gas contains a large amount of  $\text{SO}_x$  and a smaller amount of  $\text{NH}_3$ . The gas sampling tube also must be kept above  $300^\circ\text{C}$  to prevent ammonium bisulfate deposition which can cause additional analytical errors.

Although the analysis itself is fairly accurate when Methods I and II are used properly, gas sampling may cause errors since gas composition may not be homogeneous throughout a large duct. The Direct In-Gas Analysis (DIGA) method developed in the U.S. (Figure 3-69, III) may be superior from this point of view. With the DIGA method a light source is placed on one side of the duct and a detector on the other. Light passes through a pipe across the duct which is slotted to allow gas flow. This method allows quick response which eliminates sampling error. However, the accuracy of the  $\text{NH}_3$  measurement is affected by the presence not only of  $\text{SO}_2$ , but also of particulates, requiring calibrations according to their concentrations.



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## SECTION 4

### SCR FOR FLUE GAS FROM UTILITY BOILERS

#### 4.1 DESIGN AND PERFORMANCE OF SCR PLANTS

##### 4.1.1 Development of SCR for Utility Boilers

Following numerous pilot plant tests, the first prototype SCR plant was constructed in 1977 at Kansai Electric's Kainan Station. It was designed to treat one-fourth of the flue gas from an existing 450 MW oil-fired boiler by reducing  $\text{NO}_x$  from 120 ppm to about 20 ppm. The plant uses a ring-type catalyst in a fixed bed. The first commercial SCR plant for utility boilers began operation in 1978 at Chubu Electric's Chita Station. Using a pellet catalyst, the plant reduces  $\text{NO}_x$  in the flue gas of two 700 MW gas-fired boilers from 50 ppm to 10 ppm.

Since 1978, parallel flow SCR catalysts, especially the honeycomb and plate types, have significantly improved in quality and decreased in cost. In 1979 the first full scale SCR plant using a honeycomb catalyst began operation at Chugoku Electric's Kudamatsu Station. It reduced  $\text{NO}_x$  in the flue gas of an existing 375 MW oil-fired boiler from 130 to 20 ppm. All of the commercial SCR plants constructed in 1979 for utility boilers use honeycomb or plate catalysts, except for one plant which uses a tubular catalyst. Even for clean gas containing little dust, the parallel flow catalyst with a thin wall is superior to the pellet catalyst because of the lower gas pressure drop it causes.

Full-scale plants for testing a combined system of selective noncatalytic reduction (SNR) and SCR applied to existing oil-fired boilers were constructed in 1978 by Tokyo Electric and Kansai Electric. The tests were subsequently discontinued and the SNR system was removed leaving the SCR system (Section 6.3).

For coal-fired boilers, the first full scale SCR plant began operation in 1980 at Chugoku Electric's Shimonoseki Station. The station treats flue gas from an existing 175 MW boiler using a honeycomb catalyst. In 1980, another SCR plant began operation at Hokkaido Electric's Tomato-Atsuma Station. It uses a plate catalyst to treat one-fourth of the gas from a new 350 MW boiler. Seven SCR plants for coal-fired boilers began operation in 1981 and 1982.

By the end of 1982, the total SCR capacity for utility boilers will exceed 21,000 MW, including about 3,300 MW for coal-fired boilers. SCR plants with a capacity of treating more than 250,000/Nm<sup>3</sup>/hr of flue gas (75 MW equivalent) from utility boilers are listed in Table 4-1. Almost all of the coal-fired boilers which will begin operation after 1982 will need SCR, although NO<sub>x</sub> can be reduced to 160-200 ppm using combustion modification alone.

Most of the SCR plants in Japan are designed for 80-85 percent NO<sub>x</sub> removal with unreacted NH<sub>3</sub> below about 5 ppm. Although it may be possible to remove 90 percent or more of the NO<sub>x</sub>, 80-85 percent removal has been found to be the optimum level because of the smaller pressure drop, smaller amount of unreacted NH<sub>3</sub>, and lower SO<sub>2</sub>/SO<sub>3</sub> oxidation rate associated with it. Some of the SCR plants initially are using a small amount of the catalyst to remove 50-60 percent of NO<sub>x</sub> and will increase the amount of catalyst to remove 80-85 percent when needed in the future.

All of the SCR plants for utility boilers have been or will be constructed by boiler manufacturers: MHI, BHK, IHI, and KHI. MHI, the largest boiler manufacturer in Japan, builds the largest share of the SCRs; normally the SCR plant is constructed by the boiler manufacturer.

TABLE 4-1. SCR PLANTS FOR UTILITY BOILERS IN JAPAN AND THE UNITED STATES (By 1984)

| Power Company    | Station Name | Boiler No. | Fuel     | Capacity |                          | N/R            | Vendor           | Catalyst       | Start Up |
|------------------|--------------|------------|----------|----------|--------------------------|----------------|------------------|----------------|----------|
|                  |              |            |          | MW       | 1000 Nm <sup>3</sup> /hr |                |                  |                |          |
| Chubu Electric   | Chita        | 4          | Oil, gas | 700      | 2,000                    | R <sup>a</sup> | MHI <sup>c</sup> | H <sup>g</sup> | 1979     |
| "                | "            | 5          | Gas      | 700      | 1,910                    | N <sup>b</sup> | BHK <sup>d</sup> | G <sup>h</sup> | 1978     |
| "                | "            | 6          | Gas      | 700      | 1,910                    | N              | BHK              | G              | 1978     |
| "                | "            | 1          | Oil      | 375      | 1,100                    | N              |                  |                | 1983     |
| "                | Nishinagoya  | 6          | Oil      | 500      | 1,320                    | R              | IHI <sup>e</sup> | H              | 1980     |
| "                | "            | 4          | Oil      | 375      | 1,100                    | R              | BHK <sup>d</sup> | P <sup>i</sup> | 1981     |
| "                | "            | 3          | Oil      | 375      | 1,100                    | R              | BHK              | P              | 1982     |
| "                | Shinanagoya  | 3          | Oil      | 220      | 650                      | R              | MHI              | H              | 1980     |
| "                | "            | 2          | Oil      | 220      | 650                      | R              | MHI              | H              | 1981     |
| "                | "            | 5          | Oil      | 220      | 650                      | R              | MHI              | H              | 1981     |
| "                | "            | 6          | Oil      | 220      | 650                      | R              | MHI              | H              | 1981     |
| "                | Atsumi       | 3          | Oil      | 700      | 1,870                    | N              | MHI              | H              | 1980     |
| "                | "            | 4          | Oil      | 700      | 1,870                    | N              | MHI              | H              | 1981     |
| "                | Chita No. 2  | 1          | Gas      | 700      | 1,910                    | N              | BHK              | P              | 1983     |
| "                | "            | 2          | Gas      | 700      | 1,910                    | N              | IHI              | H              | 1983     |
| Chugoku Electric | Kudamatsu    | 2          | Oil      | 375      | 1,125                    | R              | IHI              | H              | 1979     |
| "                | "            | 3          | Oil      | 700      | 2,000                    | N              | IHI              | H              | 1979     |
| "                | Iwakuni      | 2          | Oil      | 350      | 1,000                    | R              | MHI              | H              | 1980     |
| "                | "            | 2          | Oil      | 500      | 1,450                    | N              | MHI              | H              | 1980     |
| "                | Shimonoseki  | 1          | Coal     | 175      | 580                      | R              | MHI              | H              | 1980     |
| "                | Shin-Ube     | 1          | Coal     | 75       | 250                      | R              | MHI              | H              | 1982     |
| "                | "            | 2          | Coal     | 75       | 250                      | R              | MHI              | H              | 1982     |
| "                | "            | 3          | Coal     | 156      | 500                      | R              | MHI              | H              | 1982     |
| "                | Mizushima    | 1          | Coal     | 125      | 400                      | R              | BHK              | P <sup>i</sup> | 1984     |
| "                | "            | 2          | Coal     | 156      | 500                      | R              | BHK              | P              | 1984     |

(Continued)

<sup>a</sup>Retrofit  
<sup>b</sup>New  
<sup>c</sup>Mitsubishi Heavy Industries  
<sup>d</sup>Babcock Hitachi  
<sup>e</sup>Ishikawajima Harima Heavy Industries  
<sup>f</sup>Kawasaki Heavy Industries

<sup>g</sup>Honeycomb  
<sup>h</sup>Granule  
<sup>i</sup>Plate  
<sup>j</sup>Tube



TABLE 4-1. SCR PLANTS FOR UTILITY BOILERS IN JAPAN AND THE UNITED STATES (By 1984) (Continued)

| Power Company       | Station Name  | Boiler No. | Fuel      | Capacity |                          | N/R            | Vendor           | Catalyst       | Start Up |
|---------------------|---------------|------------|-----------|----------|--------------------------|----------------|------------------|----------------|----------|
|                     |               |            |           | MW       | 1000 Nm <sup>3</sup> /hr |                |                  |                |          |
| Electric Power D.C. | Takehana      | 1          | Coal      | 250x1/3  | 400                      | R              | BNK              | P              | 1981     |
| "                   | "             | "          | "         | 250x1/2  | 400                      | R              | KHI <sup>f</sup> | T <sup>j</sup> | 1981     |
| "                   | "             | 3          | Coal      | 700      | 2,340                    | N              | BNK              | P              | 1983     |
| Hokkaido Electric   | Tomato-Azumai | 1          | Coal      | 350x1/4  | 280                      | N              | BNK              | P              | 1980     |
| Hokuriku Electric   | Toyama        | 2          | Oil       | 500      | 1,470                    | N              | IHI              | H              | 1980     |
| Toban Electric      | Nakoso        | 8          | Oil, Coal | 600      | 1,810                    | N <sup>b</sup> | MHI <sup>c</sup> | H <sup>g</sup> | 1982     |
| "                   | "             | 9          | Oil, Coal | 600      | 1,810                    | N              | IHI              | H              | 1983     |
| Kansai Electric     | Osaka         | 1          | Oil       | 156      | 500                      | R <sup>a</sup> | MHI              | H              | 1978     |
| "                   | "             | 2          | Oil       | 156      | 500                      | R              | MHI              | H              | 1981     |
| "                   | "             | 3          | Oil       | 156      | 500                      | R              | MHI              | H              | 1980     |
| "                   | "             | 4          | Oil       | 156      | 500                      | R              | MHI              | H              | 1980     |
| "                   | Katsun        | 1          | Oil       | 450x1/4  | 300                      | R <sup>d</sup> | BNK              | P <sup>i</sup> | 1979     |
| "                   | "             | 3          | Oil       | 600      | 1,640                    | R              | MHI              | H              | 1982     |
| "                   | "             | 4          | Oil       | 600      | 1,640                    | R              | BNK              | P              | 1981     |
| "                   | Himeji I      | 4          | Oil       | 156      | 500 <sup>k</sup>         | R              | IHI <sup>e</sup> | H              | 1978     |
| "                   | Himeji II     | 6          | Gas, oil  | 600      | 1,640                    | R              | IHI              | H              | 1981     |
| "                   | Amagasaki-    | 1          | Oil       | 156      | 470                      | R              | BNK              | P              | 1978     |
| "                   | higashi       | 2          | Oil       | 156      | 470                      | R              | BNK              | P              | 1980     |
| "                   | Amagasaki-    | 1          | Oil       | 156      | 470                      | R              | BNK              | P              | 1981     |
| "                   | No. 3         | 2          | Oil       | 156      | 470                      | R              | BNK              | P              | 1980     |
| "                   | "             | 3          | Oil       | 156      | 470                      | R              | BNK              | P              | 1980     |
| "                   | Sakaiko       | 1          | Gas, oil  | 250      | 800                      | R              | MHI              | H              | 1980     |
| "                   | "             | 2          | Gas, oil  | 250      | 800                      | "              | MHI              | H              | 1981     |
| "                   | "             | 4          | Gas, oil  | 250      | 800                      | R              | MHI              | H              | 1981     |

<sup>a</sup> Retrofit<sup>b</sup> New<sup>c</sup> Mitsubishi Heavy Industries<sup>d</sup> Babcock Hitachi<sup>e</sup> Ishikawajima Harima Heavy Industries<sup>f</sup> Kawasaki Heavy Industries<sup>g</sup> Honeycomb<sup>h</sup> Granule<sup>i</sup> Plate<sup>j</sup> Tube<sup>k</sup> Combination with SNR was tested.

(Continued)



TABLE 4-1. SCR PLANTS FOR UTILITY BOILERS IN JAPAN AND THE UNITED STATES (By 1984) (Continued)

| Power Company    | Station Name     | Boiler No. | Fuel             | Capacity 1000 |                     | N/R            | Vendor           | Catalyst       | Start Up |
|------------------|------------------|------------|------------------|---------------|---------------------|----------------|------------------|----------------|----------|
|                  |                  |            |                  | MW            | Nm <sup>3</sup> /hr |                |                  |                |          |
| Kansai Electric  | Sakaiko          | 5          | Gas, oil         | 250           | 800                 | R              | BNK              | P              | 1980     |
| "                | "                | 6          | Gas, oil         | 250           | 800                 | R              | MHI              | H              | 1979     |
| "                | "                | 7          | Gas, oil         | 250           | 800                 | R              | MHI              | H              | 1981     |
| "                | Tanagawa         | 3          | Oil              | 156           | 500                 | R              | MHI              | H              | 1981     |
| "                | "                | 4          | Oil              | 156           | 500                 | R              | MHI              | H              | 1981     |
| "                | Tanagawa II      | 2          | Oil              | 600           | 1,520               | R              | BNK              | P              | 1981     |
| "                | Kasugade         | 1          | Oil              | 156           | 470                 | R              | IHI              | H              | 1980     |
| "                | "                | 2          | Oil              | 156           | 470                 | R              | IHI              | H              | 1981     |
| "                | Aici             | 1          | Oil              | 375           | 1,030               | N <sup>b</sup> | IHI <sup>a</sup> | H <sup>d</sup> | 1982     |
| "                | "                | 2          | Oil              | 375           | 1,030               | N              | IHI              | H              | 1982     |
| "                | "                | 3          | Oil              | 375           | 1,030               | N              | IHI              | H              | 1982     |
| "                | Gobou            | 1          | Oil              | 600           | 1,600               | N              | MHI <sup>c</sup> | H              | 1984     |
| "                | "                | 2          | Oil              | 600           | 1,600               | N              | BNK <sup>d</sup> | P <sup>i</sup> | 1984     |
| "                | "                | 3          | Oil              | 600           | 1,600               | N              | MHI              | H              | 1984     |
| Kyushu Electric  | Shinkokuya       | 3          | Gas              | 600           | 1,640               | N              | MHI              | G              | 1978     |
| "                | "                | 4          | Gas              | 600           | 1,640               | N              | MHI              | G              | 1978     |
| "                | "                | 5          | Gas              | 600           | 1,640               | N              | MHI              | G              | 1982     |
| "                | Omura            | 2          | Coal             | 156           | 500                 | R <sup>a</sup> | MHI              | H              | 1982     |
| "                | Minato           | 1          | Coal             | 156           | 500                 | R              | MHI              | H              | 1983     |
| Tokoku Electric  | N. Niigata       | 2          | Oil              | 600           | 1,640               | N              | IHI              | H              | 1981     |
| "                | Sendai           | 3          | Coal             | 175           | 580                 | R              | BNK              | P              | 1982     |
| Tokyo Electric   | Yokosuka         | 4          | Oil              | 330           | 1,060 <sup>k</sup>  | R              | MHI              | H              | 1978     |
| Tokyo Electric   | Yokosuka         | 1          | COM <sup>i</sup> | 265           | 850                 | R              | MHI              | H              | 1984     |
| Tokyo Electric   | Yokosuka         | 2          | COM <sup>i</sup> | 265           | 850                 | R              | MHI              | H              | 1984     |
| "                | Oh               | 2          | Oil              | 330           | 1,060 <sup>k</sup>  | R              | IHI              | H              | 1978     |
| "                | Yokohama         | 1          | Oil              | 156           | 500 <sup>k</sup>    | R              | BNK              | P              | 1978     |
| S. Calif. Edison | Huntington Beach | 2          | Oil              | 215x1/2       | 350                 | R              | KHI              | H              | 1981     |

<sup>a</sup> Retrofit<sup>b</sup> New<sup>c</sup> Mitsubishi Heavy Industries<sup>d</sup> Babcock & Wilcox<sup>e</sup> Ishikawajima Harima Heavy Industries<sup>f</sup> Kawasaki Heavy Industries<sup>g</sup> Honeycomb<sup>h</sup> Granule<sup>i</sup> Plate<sup>j</sup> Tube<sup>k</sup> Combination with SNR was tested.<sup>l</sup> Coal-Oil Mixture

For oil- and coal-fired boilers, MHI and IHI use a honeycomb catalyst while BHK uses a plate catalyst (Figure 3-33). KHI has constructed an SCR plant for a coal-fired boiler at EPDC's Takehara Station which uses a tubular catalyst. However, KHI probably will use honeycomb catalysts for future plants.

Compared with FGD, SCR is much simpler and costs about one-third to one-fourth less. An SCR unit is also much easier to operate and does not require an operator. When applied to oil-fired boilers, SCR plants have experienced almost no problems except for ammonium bisulfate deposition in air preheaters (Section 3.6).

#### 4.1.2 Design of SCR Plants

A typical design of an SCR plant for an oil-fired utility boiler is shown in Figures 4-1 and 4-2. Flue gas leaving the boiler economizer outlet at 300-400°C is mixed with ammonia and sent into an SCR reactor. Although one reactor may be adequate to treat flue gas from a 700 MW boiler, two reactors in parallel also may be used with a boiler larger than 400 MW. The flue gas leaving the reactor is passed through an air preheater, an ESP, and then a scrubber, if necessary. The flue gas from an oil-fired boiler may be passed horizontally or up through the reactor while that from a coal-fired boiler must pass downward to eliminate dust plugging.

Figure 4-3 shows an example of an ammonia injection system. Generally, the ammonia flow rate is controlled by the flue gas flow rate and the incoming NO<sub>x</sub> concentration. In a large boiler it is difficult to precisely measure the flue gas flow rate. The steam flow rate to the turbine is used as a measure of the amount of fuel being burned and the combustion gas produced. This control method can be finely tuned using the outlet NO<sub>x</sub> level as a feedback signal.

When a boiler is operated at a low load, a low-temperature economizer outlet gas is produced. When this happens ammonium bisulfate deposits may

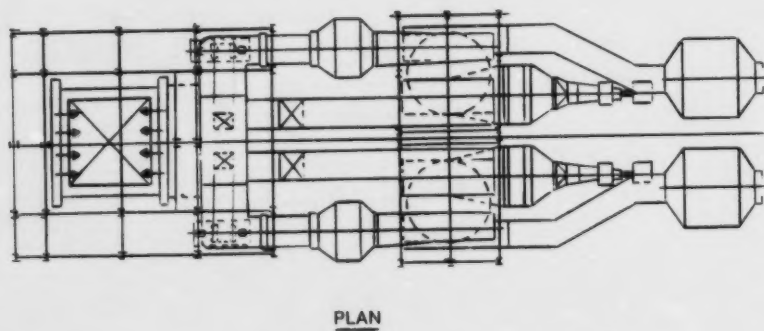
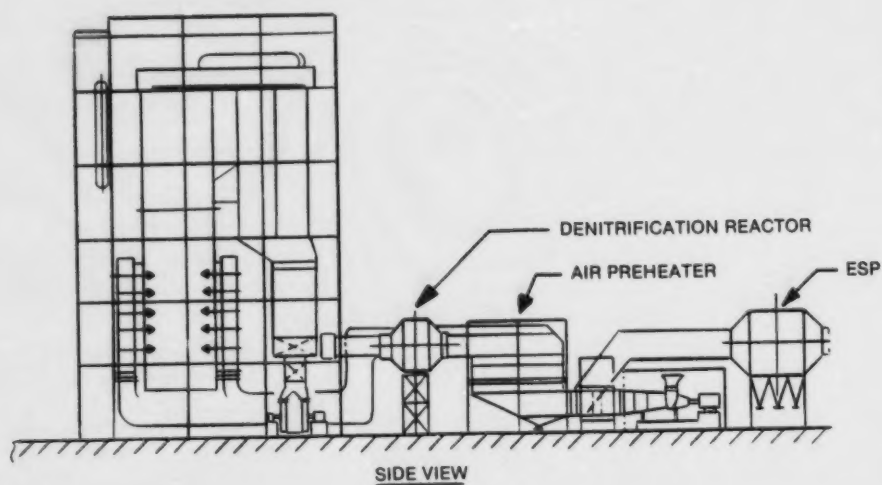


Figure 4-1 SCR Plant Layout. (IHI)

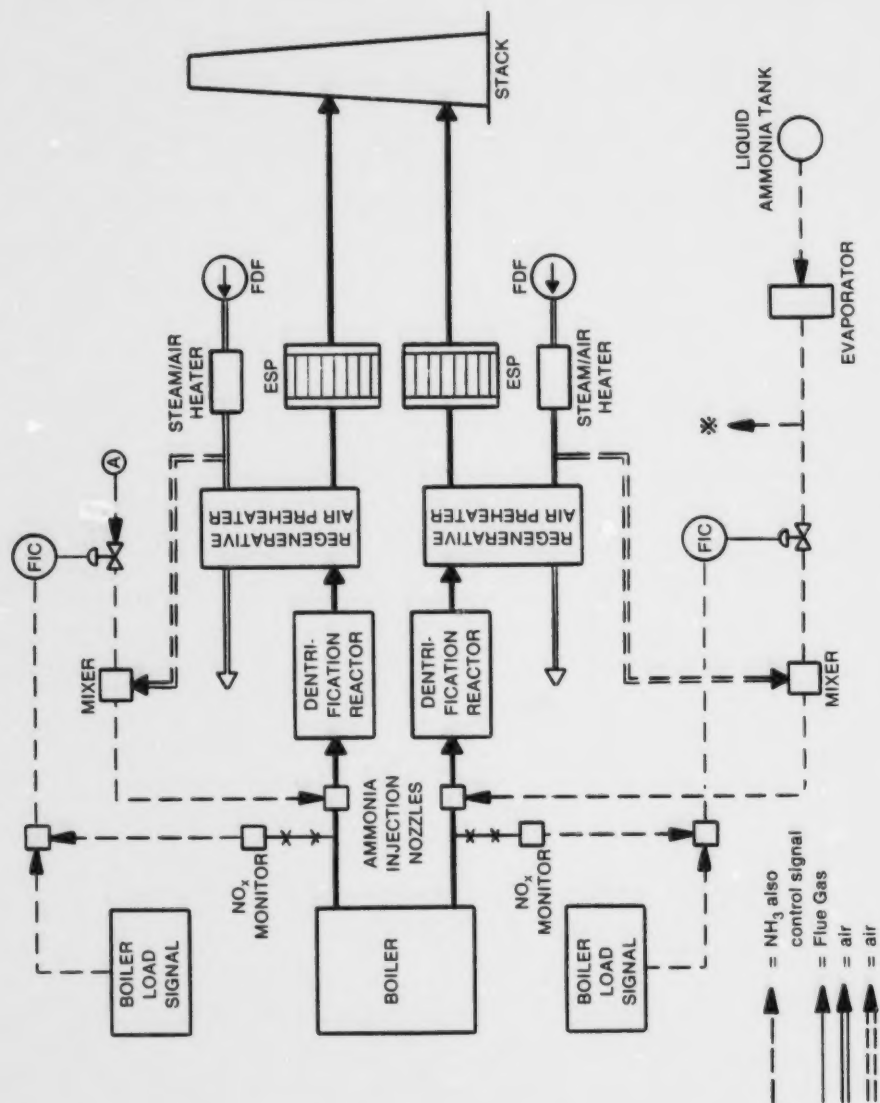


Figure 4-2 Flowsheet for Standard Boiler Denitrification Equipment Used with Heavy Oil Combustion Gas. (IHI)

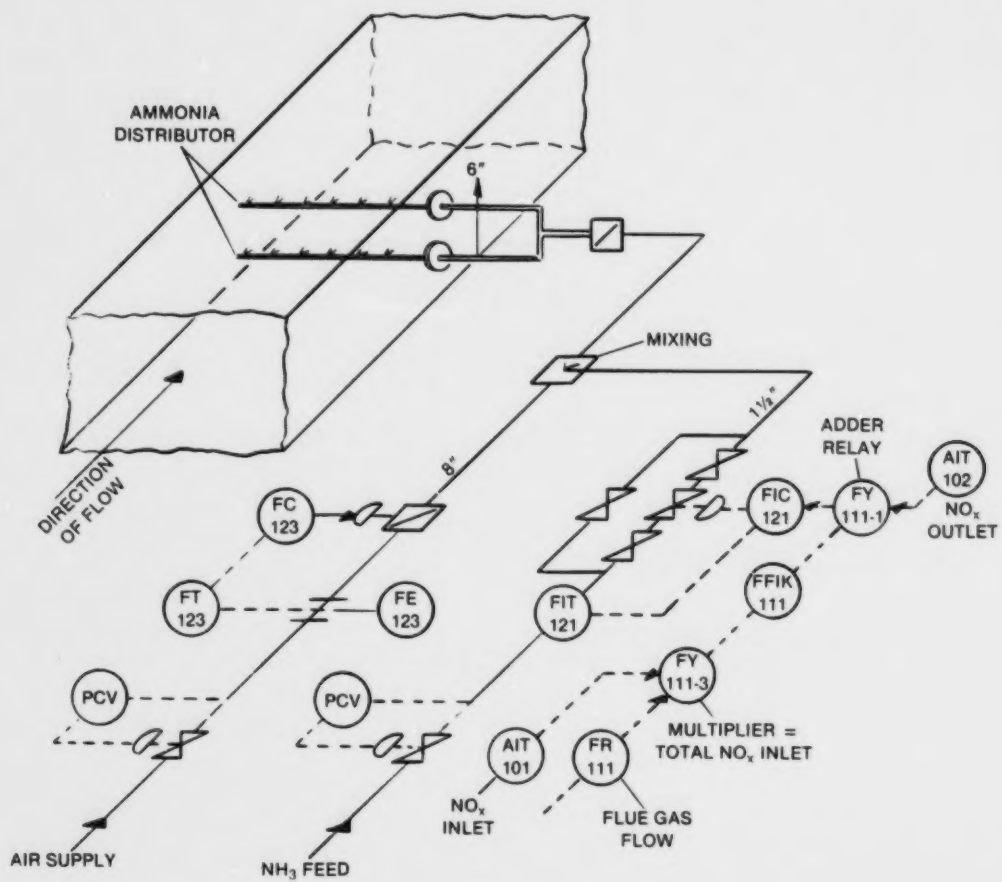


Figure 4-3 Ammonia Injection System. (1)



decrease the SCR catalyst's activity (Section 3.7.2). To eliminate the problem, a gas heating device can be installed on some boilers. The gas is heated either by an economizer by-pass as shown in Figure 4-4A or by modifying the economizer as shown in Figure 4-4B. The modified economizer has two heat transfer compartments, one with high efficiency and the other with low efficiency. Most of the gas is passed through the low-efficiency compartment at the low load to maintain the gas temperature above a desired level. Using such a device lowers the heat recovery efficiency at the economizer but allows the heat to be recovered by the air preheater downstream of the SCR reactor, thus avoiding a loss of energy.

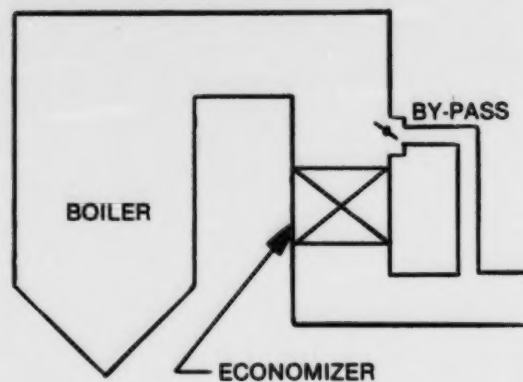
The SCR reactor usually has a soot blowing system which cleans the catalyst using hot air or steam. An example of a soot blowing system is shown in Figure 4-5. However, a soot blower has not been used with most of the reactors which utilize parallel flow catalysts.

#### 4.1.3 SCR Performance

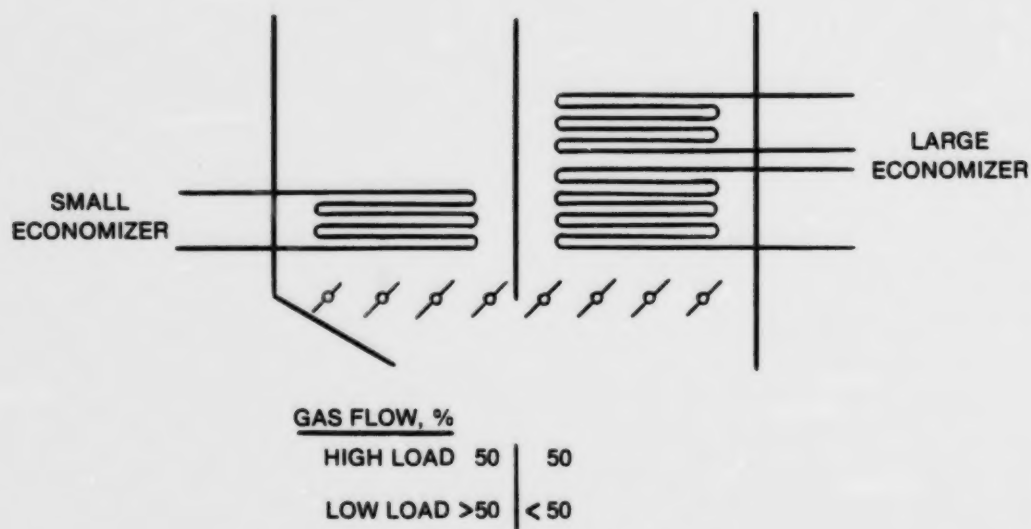
The typical performance of an SCR unit used with a utility boiler is shown in Figure 4-6. When the boiler load is reduced, the gas temperature is substantially lowered and the  $\text{NO}_x$  removal efficiency remains almost the same. In this situation, the reduced flue gas volume results in a smaller SV, or longer reaction time. The  $\text{SO}_2$  oxidation ratio also remains essentially the same despite a decrease in the boiler load. However, both unreacted  $\text{NH}_3$  and pressure drop are lowered with the load.

Below a certain temperature, ammonium bisulfate (or related compounds) deposits on the catalyst and lowers catalytic activity. The critical temperature depends upon the inlet concentrations of  $\text{SO}_x$  and  $\text{NH}_3$  and on the degree of  $\text{SO}_2$  oxidation by the catalyst. For a flue gas from a low-sulfur oil, the critical temperature is typically around  $300^\circ\text{C}$ ; for flue gases from coal and high-sulfur oil, it is  $20\text{--}40^\circ\text{C}$  higher. If the gas temperature remains below the critical temperature for a few hours a day (for example during the low boiler load at midnight) and is kept around  $400^\circ\text{C}$  for the remainder of the





A: ECONOMIZER BY-PASS



B: SPLIT ECONOMIZER ARRANGEMENT (3)

Figure 4-4 Economizer Outlet Temperature Adjustments.

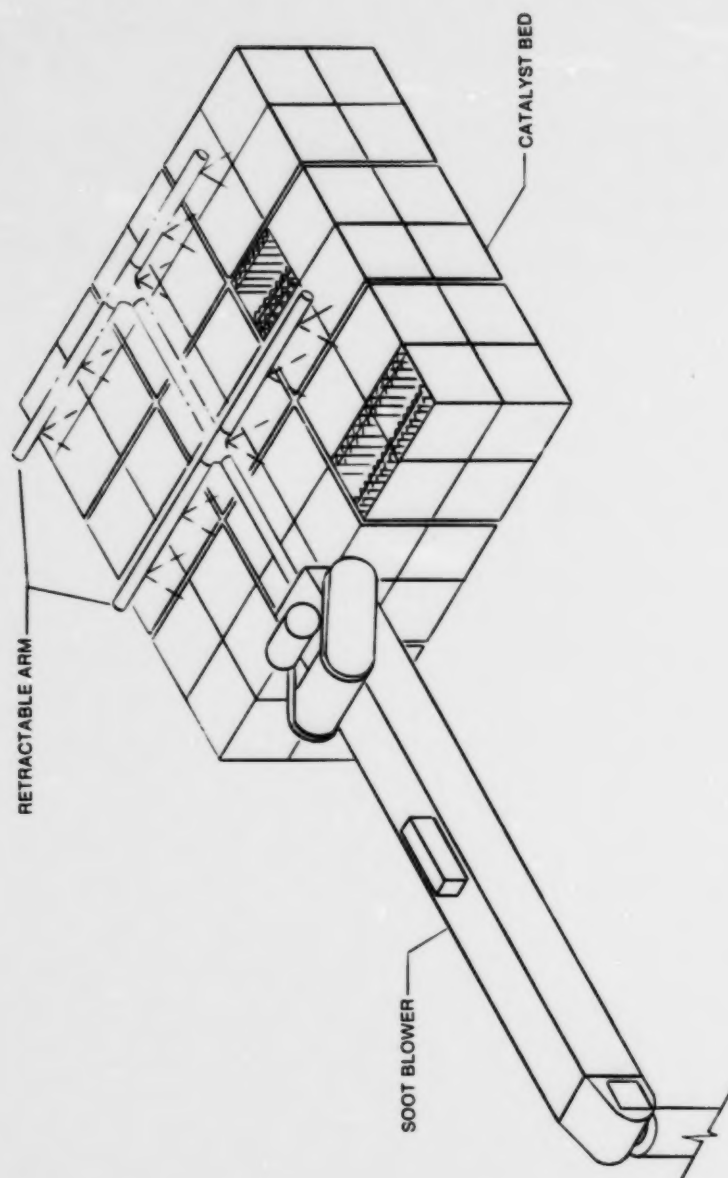


Figure 4-5 Soot Blower Used with an SCR Reactor. (1)

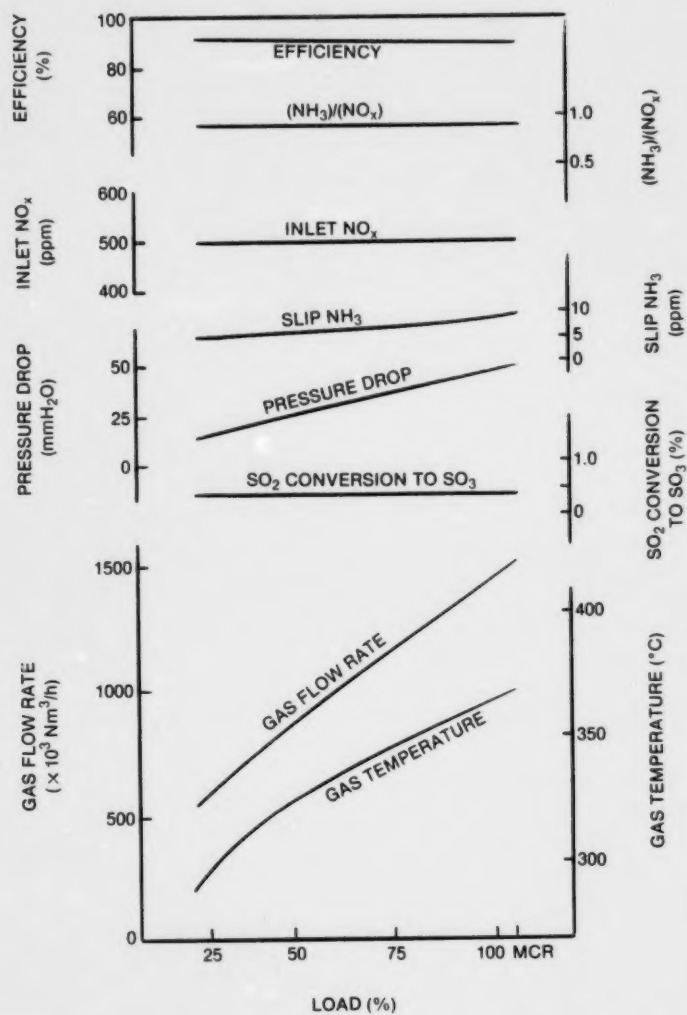


Figure 4-6 Expected Performance of an SCR Unit for a Utility Boiler. (2)

day, the small amount of bisulfate formed on the catalyst at the low temperature will be removed at around 400°C. Thus, there will not be much of an adverse effect on the overall NO<sub>x</sub> removal efficiency. If the gas temperature is maintained below the critical temperature for a longer period, the bisulfate deposition may become pronounced. To eliminate this problem the gas temperature should be maintained above a certain level, as previously described in Section 4.1.2.

For most utility boiler SCR plants, an NH<sub>3</sub>/NO<sub>x</sub> mole ratio of 0.83-0.90 has been used to remove 80-85 percent of NO<sub>x</sub> while maintaining unreacted NH<sub>3</sub> below 10 ppm. Soot blowing is seldom used and thus no operator is needed for routine operation.

The remaining problem associated with SCR is ammonium bisulfate deposition in the air preheater. In most of the SCR plants the problem has been solved by maintaining unreacted NH<sub>3</sub> below 5 ppm, and using combustion control to reduce SO<sub>2</sub>, and low-oxidation catalysts. Some of the plants also use improved air heater elements and intensive soot blowing to remove the deposits. A small amount of ammonium bisulfate may still deposit despite these practices, but it does not affect SCR operation. If necessary, the deposits can be removed when the boiler is shut down for its annual maintenance; in Japan larger boilers are required by law to perform this yearly maintenance.

Water washing also has been used to remove the bisulfate deposits. About 24 hours must be allowed for washing, which includes time for cooling, washing, and drying. When water washing is necessary two or more times a year, one of the two parallel air preheaters is shut down for each washing while the boiler operates at a half load using the other air preheater. Recently a new technology - thermal cleaning - was developed for air preheater cleaning (Section 4.3.4).

## 4.2 SCR PLANTS OF CHUBU ELECTRIC POWER COMPANY

### 4.2.1 Introduction

Chubu Electric Power Company is the third largest utility company in Japan with power stations located in the Chubu area which is between the Kanto Area (including Tokyo) and the Kansai Area (including Osaka). Since most of its steam power generating stations are close to cities and industrial regions, extensive air pollution countermeasures have been taken. These include FGD and the use of low-sulfur fuels for  $\text{SO}_x$  abatement, and combustion modification, SCR, and selective noncatalytic reduction (SNR) for  $\text{NO}_x$  abatement.

Chubu Electric's SCR plants are shown in Table 4-2. Since the three plants constructed at the Chita Station in 1978 and 1980 worked so successfully, Chubu Electric installed nine more units in 1980 and 1981 and will construct four more in 1982 and 1983.

### 4.2.2 Chita Power Station

The Chita Power Station, near Nagoya City (population, 2 million), has six boilers (Table 4-3) which use the most advanced  $\text{NO}_x$  control systems for utility boilers in Japan.

Extensive combustion modification has been applied to the boilers at the Chita Station, including staged combustion, flue gas recirculation, low excess air combustion, and low  $\text{NO}_x$  burners. The 350 ppm  $\text{NO}_x$  concentration in flue gas from oil-fired boilers is reduced to about 100 ppm (a 70 percent removal rate) by combustion modification.

The No. 5 and No. 6 LNG-fired boilers began operation in 1978. In order to obtain permits from the local authorities (Aichi Prefecture and Chita City) for the construction of two new boilers, Chubu Electric promised to use LNG fuel and to install SCR units to minimize  $\text{NO}_x$  emissions. In addition, Chubu Electric installed an SNR system for the No. 2 boiler and an SCR unit for the

TABLE 4-2. CHUBU ELECTRIC'S SCR PLANTS

| Station        | Boiler<br>No. | Capacity<br>(MW) | N/R* | Fuel     | NO <sub>x</sub> (ppm)<br>Inlet <sup>1</sup> Outlet | Removal<br>(Percent) | Completion<br>Date |
|----------------|---------------|------------------|------|----------|----------------------------------------------------|----------------------|--------------------|
| Chita          | 5             | 700              | N    | Gas      | 50 10                                              | 80                   | Mar. 1978          |
|                | 6             | 700              | N    | Gas      | 50 10                                              | 80                   | Apr. 1978          |
| Nishinagoya    | 4             | 700              | R    | Gas, oil | 100 20                                             | 80                   | Mar. 1980          |
|                | 1             | 375              | R    | Oil      | 135 70                                             | 50                   | Dec. 1982          |
|                | 6             | 500              | R    | Oil      | 100 20                                             | 80                   | Jul. 1980          |
|                | 4             | 375              | R    | Oil      | 100 20                                             | 80                   | Mar. 1981          |
| Atsumi         | 3             | 375              | R    | Oil      | 100 20                                             | 80                   | Jan. 1982          |
|                | 3             | 700              | N    | Oil      | 80 16                                              | 80                   | May 1981           |
|                | 4             | 700              | N    | Oil      | 80 16                                              | 80                   | June 1981          |
|                | 3             | 220              | R    | Oil      | 75 50                                              | 33                   | Sept. 1980         |
| Shinnagoya     | 2             | 220              | R    | Oil      | 90 60                                              | 33                   | Apr. 1981          |
|                | 5             | 220              | R    | Oil      | 75 50                                              | 33                   | Sept. 1981         |
|                | 6             | 220              | R    | Oil      | 85 60                                              | 29                   | May 1981           |
|                | 1             | 700              | N    | Gas      | 50 10                                              | 80                   | May 1983           |
| Chita<br>No. 2 | 2             | 700              | N    | Gas      | 50 10                                              | 80                   | Jul. 1983          |

\*New or retrofit.



TABLE 4-3. CHITA STATION BOILER AND NO<sub>x</sub> ABATEMENT DATA

|                                                       | No. 1            | No. 2            | No. 3  | No. 4            | No. 5            | No. 6            |
|-------------------------------------------------------|------------------|------------------|--------|------------------|------------------|------------------|
| Boiler                                                |                  |                  |        |                  |                  |                  |
| Capacity, MW                                          | 375              | 375              | 500    | 700              | 700              | 700              |
| Boiler Maker                                          | MHI <sup>a</sup> | MHI              | MHI    | MHI              | BHK <sup>b</sup> | BHK <sup>b</sup> |
| Operation Start-up                                    | 1965             | 1966             | 1967   | 1974             | 1978             | 1978             |
| Fuel                                                  | Oil              | Oil              | Oil    | Oil, LNG         | LNG              | LNG              |
| NO <sub>x</sub> , ppm                                 | 120-140          | 120-140          | 90-100 | 95-100           | 35-50            | 35-50            |
| NO <sub>x</sub> limitation, ppm                       | 150              | 100              | 105    | 20               | 11               | 11               |
| Denitrification Plant                                 |                  |                  |        |                  |                  |                  |
| Process                                               | -                | SNR <sup>c</sup> | -      | SCR <sup>d</sup> | SCR <sup>d</sup> | SCR <sup>d</sup> |
| Constructor                                           | -                | MHI              | -      | MHI              | Hitachi          | Hitachi          |
| Completion                                            | -                | 1977             | -      | 1980             | 1978             | 1978             |
| NO <sub>x</sub> Concentration<br>after treatment, ppm | -                | 80-100           | -      | 15-20            | 7-10             | 7-10             |
| NH <sub>3</sub> Emitted, ppm                          | -                | 10-15            | -      | Below 5          | Below 5          | Below 5          |

<sup>a</sup>Mitsubishi Heavy Industries<sup>b</sup>Babcock-Hitachi<sup>c</sup>Selective noncatalytic reduction<sup>d</sup>Selective catalytic reduction

TABLE 4-4. EMISSION LIMITS AT THE CHITA POWER STATION

| Item                    | Regulation            | Compliance Technique                                                                                               |
|-------------------------|-----------------------|--------------------------------------------------------------------------------------------------------------------|
| Water                   |                       |                                                                                                                    |
| COD, mg/L               | $\leq 10$             | • Chemical treatment                                                                                               |
| TSS, mg/L               | $\leq 15$             |                                                                                                                    |
| Oil, mg/L               | $\leq 1$              | • Rainwater to oil separator                                                                                       |
| pH                      | 5.8 - 8.6             |                                                                                                                    |
| Air                     |                       |                                                                                                                    |
| NO <sub>x</sub>         | As shown in Table 4-1 | • Combustion modifications (controlled mixing and OFA)<br>• SCR with NH <sub>3</sub><br>• SNR with NH <sub>3</sub> |
| SO <sub>2</sub>         | -                     | • Low sulfur fuel                                                                                                  |
| Ash, mg/Nm <sup>3</sup> | $\leq 20$             | • ESP's on boilers 1, 2, 3, and 4                                                                                  |
| Noise, phones           | $\leq 50$             | • Walls around transformer<br>• FD fan insulated<br>• Valves covered                                               |

No. 4 boiler so that the total  $\text{NO}_x$  emissions would not increase with the addition of boilers No. 5 and No. 6. The SNR system is described in Section 6.2.4.

Table 4-4 shows the water,  $\text{NO}_x$ ,  $\text{SO}_2$ , particulate, and noise emission limits which apply to the Chita Power Station.

#### 4.2.3 SCR Units at the Chita Station

Two full scale SCR units for the new No. 5 and No. 6 700-MW LNG-fired boilers were constructed by Babcock-Hitachi using a pellet catalyst supplied by Hitachi Ltd. (Table 4-5). Flue gas (1,900,000  $\text{Nm}^3/\text{hr}$  per boiler) from the boiler economizer at  $350^\circ\text{C}$  (full load) and  $290^\circ\text{C}$  (250 MW load) is injected with air-diluted  $\text{NH}_3$  and sent into two parallel reactors. Each reactor measures  $10.5 \times 11.5 \times 12.0 \text{ m}$  and has four 11 cm-deep layers of a pellet catalyst (Figure 4-7). The flue gas passes through one of the layers in which the SV is  $20,000 \text{ hr}^{-1}$ . Because of good combustion control the inlet  $\text{NO}_x$  concentration is only 35-45 ppm. By adding about 0.9 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$ , over 80 percent  $\text{NO}_x$  removal is attained while unreacted  $\text{NH}_3$  is maintained below 5 ppm. The plant has operated without problems since its startup in April 1978. Since that time the catalyst has not been changed; a catalyst life of over 5 years is expected. The installation cost for the plant was 2400 yen/kW including the initial charge for the catalyst.

TABLE 4-5. DATA SUMMARY ON BABCOCK-HITACHI SCR SYSTEM -  
No. 5 and No. 6 BOILER, CHITA POWER STATION

|                                      |              |
|--------------------------------------|--------------|
| Reactors per unit                    | 2            |
| Catalyst Type                        | Pellet       |
| Catalyst Size, mm                    | 5 x 5        |
| $\text{NH}_3:\text{NO}_x$ Mole Ratio | 0.9          |
| $\text{NO}_x$ Removal, design, %     | 80           |
| $\text{NO}_x$ Inlet, ppm             | 35-45        |
| $\text{NO}_x$ Outlet, ppm            | 7-9          |
| Catalyst Manufacturer                | Hitachi Ltd. |

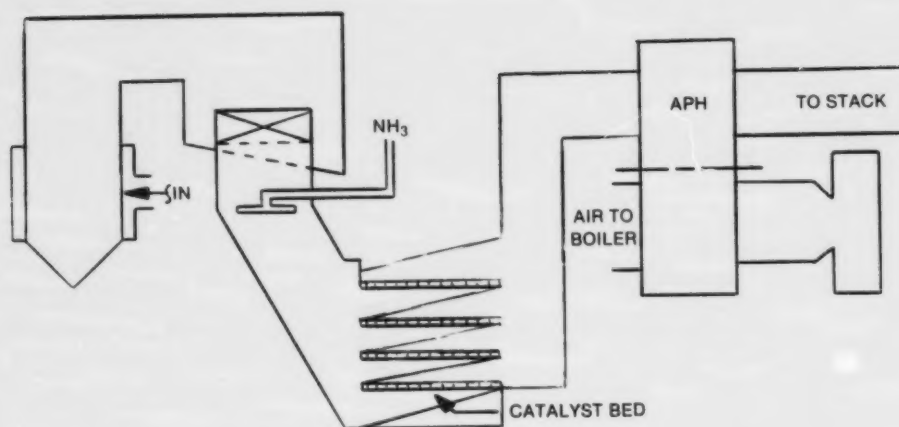


Figure 4-7 SCR Reactor and Catalyst Bed. (No. 5 and No. 6 Boilers, Chita Station) (3)

The SCR unit for the existing No. 4 boiler at the Chita Station was supplied by MHI and began continuous operation in March 1980. The design data for the unit are shown in Table 4-6. The unit's reactor and catalyst arrangements are shown in Figure 4-8. Within the reactor, a coated hexagonal honeycomb catalyst with a 6.8 mm channel diameter and a 1.2 mm wall thickness, is stacked in four stages. Each stage consists of two layers of catalyst packages; each package contains 50 elements.

Since startup, the SCR unit has operated without problems and has succeeded in reducing  $\text{NO}_x$  from about 100 ppm to about 18 ppm by using about 0.85 mol  $\text{NH}_3$  to each mol of  $\text{NO}_x$ . Unreacted  $\text{NH}_3$  has been maintained at 1-2 ppm. For fuel, the No. 4 boiler uses both low-sulfur oil and LNG, mostly the latter. There has been no ammonium bisulfate problem with the air preheater because of the low  $\text{SO}_x$  content of the flue gas and the very low level of leakage  $\text{NH}_3$ .

The cost of this SCR installation is 2.5 billion yen (3,430 yen/kW) and therefore is relatively expensive. This is a result of the required retrofitting of extensive ductwork. The unit also uses a relatively large amount of catalyst ( $\text{SV } 5,430 \text{ hr}^{-1}$ ) to treat flue gas from oil containing  $\text{SO}_x$  and particulates, with a low level of leakage  $\text{NH}_3$ .

#### 4.2.4 SCR Plants at Other Stations

In 1980 and 1981, eight SCR plants were completed at three of Chubu Electric's stations - Nishinagoya, Atsumi, and Shinnagoya - as shown in Table 4-2.

Two of the SCR plants at Atsumi are used with new 700-MW oil-fired boilers. These plants have square (grid) honeycomb catalysts with a 7 mm pitch (channel diameter plus wall thickness) and an SV of  $5,200 \text{ hr}^{-1}$ . A low-sulfur oil containing about 0.2 percent sulfur is burned with combustion modification using a low- $\text{NO}_x$  burner to yield a flue gas containing about 100 ppm  $\text{SO}_x$  and 80 ppm  $\text{NO}_x$ . The gas is treated by SCR to reduce  $\text{NO}_x$  below 16 ppm. These plants have not experienced any problems to date.

TABLE 4-6. DESIGN DATA FOR THE MHI SCR SYSTEM USED WITH THE NO. 4  
BOILER AT THE CHITA POWER STATION (3)

|                                             |                        |
|---------------------------------------------|------------------------|
| <u>General</u>                              |                        |
| Gas Volume, Nm <sup>3</sup> /hr             | 1,960,000              |
| NO <sub>x</sub> Removal, percent            | 80                     |
| NO <sub>x</sub> Inlet, ppm                  | 100                    |
| NO <sub>x</sub> Outlet, ppm                 | < 20                   |
| <u>Reactor</u>                              |                        |
| Temperature, °C                             | 388                    |
| <u>NH<sub>3</sub></u>                       |                        |
| NH <sub>3</sub> :NO <sub>x</sub> Mole Ratio | 0.9                    |
| NH <sub>3</sub> Outlet, ppm                 | < 10                   |
| <u>Catalyst</u>                             |                        |
| Space Velocity, hr <sup>-1</sup>            | 5430                   |
| Material                                    | Transition Metal Oxide |
| Shape                                       | Hexagonal Honeycomb    |
| Pitch, mm                                   | 8                      |
| Manufacturer                                | NGK                    |



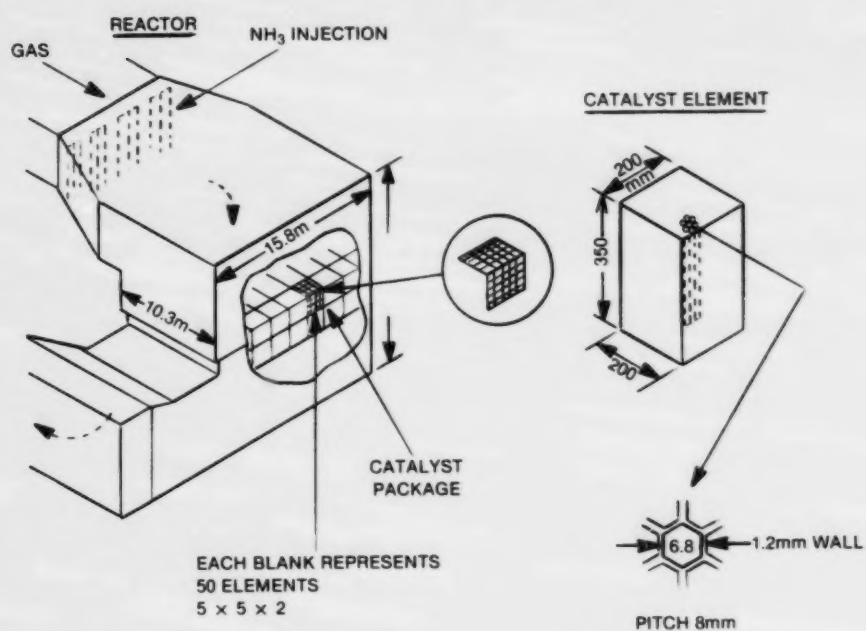
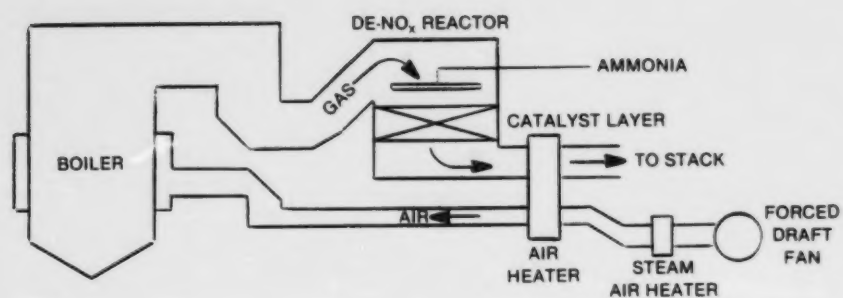


Figure 4-8 SCR Catalyst and Reactor Arrangement. (No. 4 Boiler, Chita Station) (3)

The five other SCR plants are applied to existing boilers; all use honeycomb catalysts. Those at the Nishinagoya Station achieve an 80 percent NO<sub>x</sub> removal rate, while those at the Shinnagoya Station are designed for about 30 percent NO<sub>x</sub> removal and use a smaller amount of catalyst placed in the existing duct between the boiler economizer and the air preheater. All of these SCR plants have operated without problems.

#### 4.3 SCR UNITS AT KUDAMATSU STATION, CHUGOKU ELECTRIC

##### 4.3.1 Introduction

Chugoku Electric's Kudamatsu Station is located near the Tokuyama Industrial Complex and has three oil-fired boilers as shown in Table 4-7.

TABLE 4-7. BOILERS AT THE KUDAMATSU STATION

| Boiler No. | Capacity<br>(MW) | Year of<br>Completion | NO <sub>x</sub><br>(ppm) | NO <sub>x</sub> allowed |                       |
|------------|------------------|-----------------------|--------------------------|-------------------------|-----------------------|
|            |                  |                       |                          | (ppm)                   | (Nm <sup>3</sup> /hr) |
| 1          | 156              | 1964                  | 140-160                  | 160                     | 70                    |
| 2          | 375              | 1973                  | 130-160                  | 32                      | 34                    |
| 3          | <u>700</u>       | 1979                  | 110-130                  | 26                      | <u>50</u>             |
| TOTAL      | 1,231            |                       |                          |                         | 154                   |

The No. 1 boiler was completed in 1964 and the No. 2 boiler in 1973. In order to obtain a construction permit for the No. 3 boiler, Chugoku Electric agreed to maintain total NO<sub>x</sub> emissions below 154 Nm<sup>3</sup>/hr for the entire station. To do this, SCR plants were installed not only for the No. 3 boiler but also to remove 80 percent of NO<sub>x</sub> from the No. 2 boiler (Table 4-7).

IHI constructed both the boilers and the SCR units at Kudamatsu. A honeycomb catalyst (square) is used in the SCR units. The SCR unit for the No. 2 boiler has a single reactor and began operation in April 1979. The No.

3 boiler's SCR unit has two reactors in parallel and began operation in September 1979 when the boiler also began operation.

Chugoku Electric also made agreements with the local government regarding  $\text{SO}_x$  and particulate emissions from the Kudamatsu Station. Emissions of  $\text{SO}_x$  must be maintained below  $373 \text{ Nm}^3/\text{hr}$  by using low-sulfur oils --- 0.8 percent S for the No. 1 boiler and 0.2-0.25 percent S for Nos. 2 and 3. Particulate emissions from the station must be maintained below  $20 \text{ mg}/\text{Nm}^3$  and below  $68.6 \text{ kg}/\text{hr}$  by using combustion control and ESP.

#### 4.3.2 SCR Units

Flowsheets for the No. 2 SCR unit are presented in Figures 4-9 and 4-10; SCR system specifications are presented in Table 4-8. Figure 4-9 also gives the timetable for the retrofit construction; about one year was required for the SCR installation. New ducts were connected to the existing economizer and air preheaters during the annual boiler shutdown period in February and March 1979. The flowsheet of the SCR units for the No. 3 boiler is similar to the flowsheets in Figures 4-1 and 4-2.

The reactors in the SCR units each have two layers of a square ceramic honeycomb catalyst with horizontal gas flow as shown in Figure 4-11. The catalyst was produced by Sakai Chemical and Catalyst and Chemicals, Inc. Pilot plant tests by IHI indicate that the catalysts produced by the two companies meet the specifications equally well.

The  $275\text{--}380^\circ\text{C}$  flue gas from the boiler economizer is injected with ammonia and introduced into the reactor. The gas is then sent through an air preheater and ESP. In the SCR plant for the existing No. 2 boiler, induced fans were installed to compensate for the pressure drop caused by the SCR reactor. The plant for the new No. 3 boiler does not have a fan.

TABLE 4-8. SCR PLANT SPECIFICATIONS (KUDAMATSU STATION, CHUGOKU ELECTRIC)

|                                                    | No. 2 Boiler             | No. 3 Boiler             |
|----------------------------------------------------|--------------------------|--------------------------|
| New or retrofit                                    | Retrofit                 | New                      |
| Power generation capacity, MW                      | 375                      | 700                      |
| Flue gas volume, Nm <sup>3</sup> /hr               | 1,050,000                | 1,900,000                |
| Number of SCR reactors                             | 1                        | 2                        |
| Type of catalyst                                   | Honeycomb                | Honeycomb                |
| Number of catalyst layers                          | 2                        | 2                        |
| Space velocity, SV <sup>-1</sup>                   | 5,500                    | 5,500                    |
| Catalyst volume, m <sup>3</sup>                    | 190                      | 347                      |
| Flue gas temperature, °C                           | 275-385                  | 275-380                  |
| Type of fuel                                       | Heavy oil                | Heavy oil                |
| Sulfur content of oil, %                           | 0.25                     | 0.25                     |
| Inlet NO <sub>x</sub> , ppm (O <sub>2</sub> 4%)    | 150-160                  | 110-130                  |
| NH <sub>3</sub> /NO <sub>x</sub> mole ratio        | 0.90 (0.85) <sup>a</sup> | 0.90 (0.85) <sup>a</sup> |
| NO <sub>x</sub> removal, %                         | 80 (81-83) <sup>a</sup>  | 80 (81-83) <sup>a</sup>  |
| Leak NH <sub>3</sub> , ppm                         | 10 (4-6) <sup>a</sup>    | 10 (6-8) <sup>a</sup>    |
| Catalyst life, year                                | 1 (3) <sup>a</sup>       | 1 (3) <sup>a</sup>       |
| Pressure drop through reactor, mm H <sub>2</sub> O | 102 (70) <sup>a</sup>    | 102 (70) <sup>a</sup>    |
| Start-up                                           | April 1979               | Sept. 1979               |

<sup>a</sup>Figures in parentheses are actual ones.

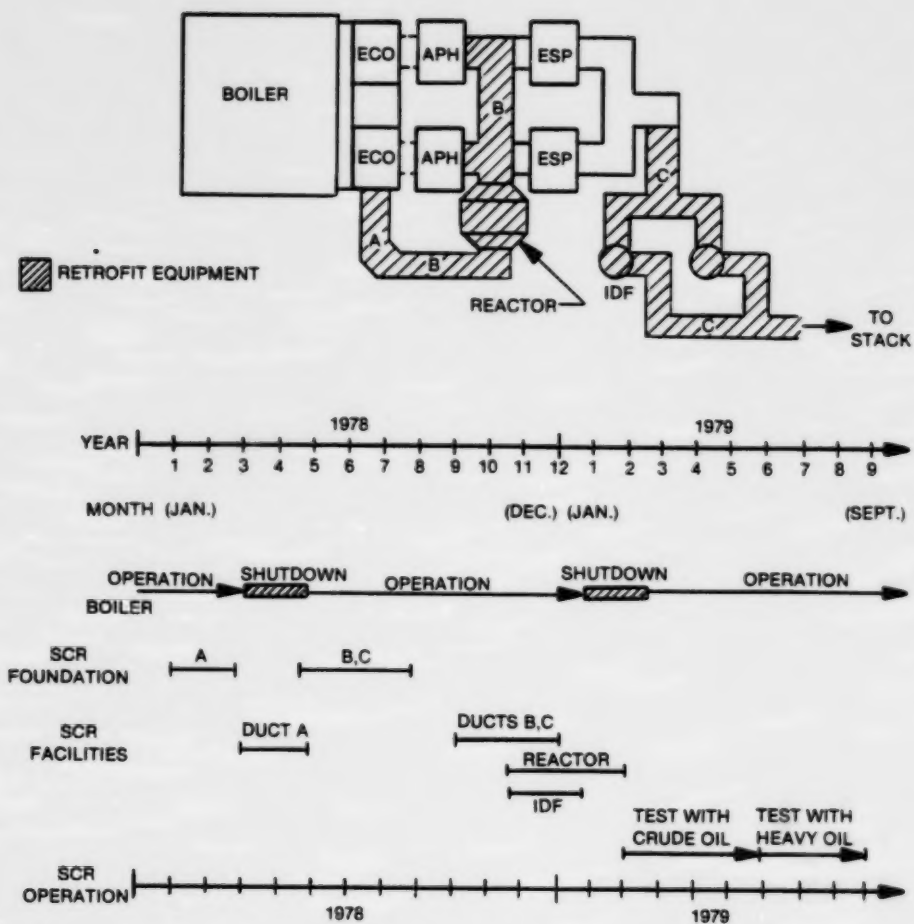


Figure 4-9 Retrofit Construction of the SCR System for the No. 2 Boiler at Kudamatsu Station.

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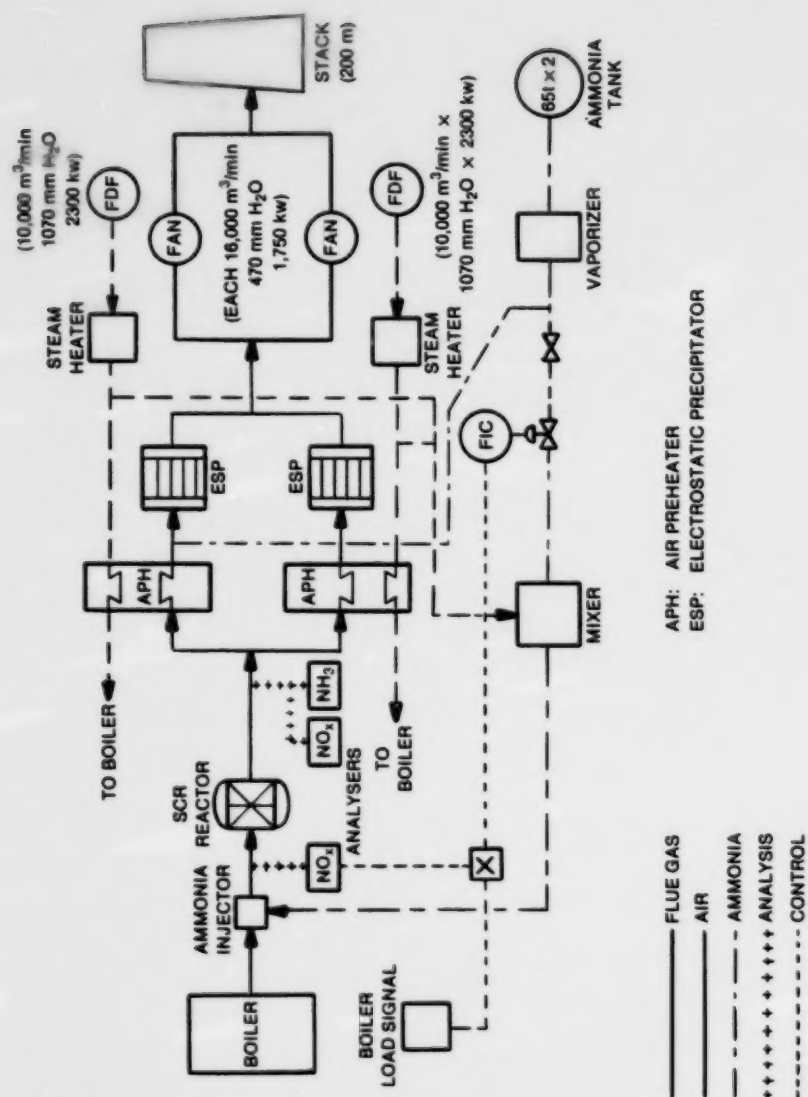


Figure 4-10 Flowchart of the SCR System for the No. 2 Boiler at Kudamatsu Station.

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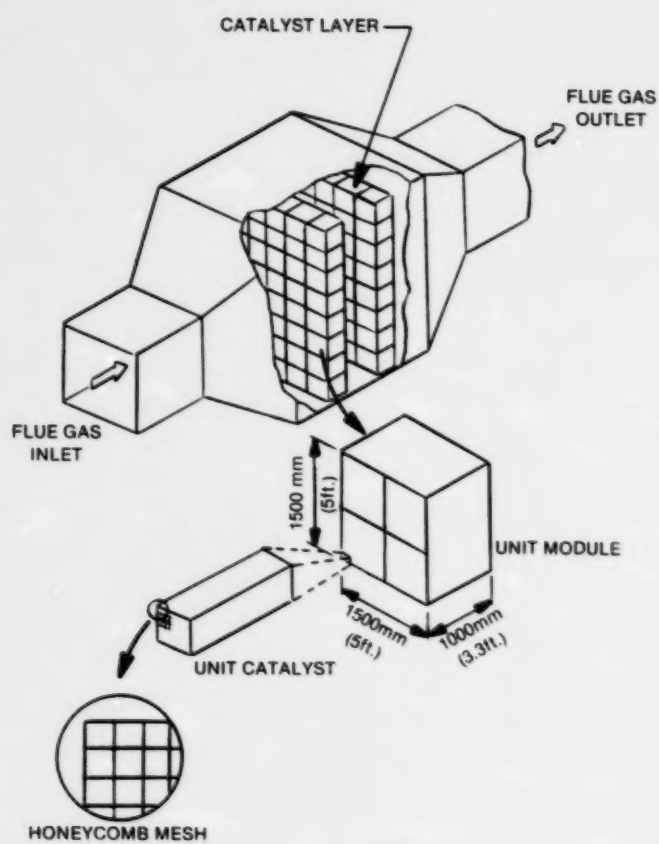


Figure 4-11 Fixed Bed Reactor for Oil-Fired Applications. (horizontal gas flow)

The correct amount of ammonia that should be injected is determined by measuring the boiler load and the inlet  $\text{NO}_x$  concentration. Outlet  $\text{NO}_x$  and ammonia concentrations are also measured to trim the system.  $\text{NO}_x$  concentrations are measured by chemiluminescence and the outlet  $\text{NH}_3$  concentration after  $\text{NO}$  conversion is continuously analyzed by catalytic oxidation (Section 3.7.6). Since this method of  $\text{NH}_3$  analysis is not highly reliable, manual analysis is periodically used for calibration.

#### 4.3.3 SCR System Performance

IHI guarantees that the  $\text{NO}_x$  removal efficiency of its SCR systems will be over 80% if an  $\text{NH}_3/\text{NO}_x$  mole ratio of 0.9 is used for more than a year. By using a mole ratio of 0.9, an 85-87%  $\text{NO}_x$  removal efficiency was attained initially at Kudamatsu. For normal operation, a mole ratio of 0.85 has been used for both systems. Currently the  $\text{NO}_x$  removal efficiency of the system is 81-82%, while in 1980 it was 82-83%. Unreacted  $\text{NH}_3$  has been maintained at about 5 ppm. Based on these results the catalyst life is expected to be more than 4 years.

At a boiler load of one-third, the economizer outlet gas temperature drops to 275°C. When the boiler load goes below one-third, ammonia injection is discontinued. At this low boiler load level the  $\text{NO}_x$  concentration is already low enough to meet the established emission limit.

The pressure drop of the flue gas is 50-60 mm  $\text{H}_2\text{O}$  through the catalyst beds and nearly 100 mm  $\text{H}_2\text{O}$  through the entire SCR system, including the reactor and the connecting ducts. No increase in the pressure drop has been noticed during the more than 3-year operation period. Soot blowing systems have been installed for the reactors but have not been used because the catalyst beds have remained clean.

The No. 1 and No. 2 boilers at the Kudamatsu Station are operated by 10 persons per shift while the No. 3 boiler is operated by 4 persons per shift. No additional personnel are needed to operate the SCR system. If necessary,

the catalyst will be replaced during the annual maintenance shutdown of the boiler.

Ammonia consumption is 80-150 t/month for the two SCR plants. Two 65-ton ammonia tanks have been installed at the station. Prior to the application of SCR, ammonia was injected into the flue gas as it left the air preheater. This was done in order to neutralize the sulfuric acid mist and to prevent the corrosion of the ESP. It produced a flue gas containing nearly 10 ppm  $\text{NH}_3$ .

The operation of the SCR units at Kudamatsu has been trouble-free except for the ammonium bisulfate problem in the air preheater which is described in the following section.

#### 4.3.4 Ammonium Bisulfate Deposition in the Air Preheater

The flue gases from the No. 2 and No. 3 boilers contain about 1 ppm  $\text{SO}_2$  with about 100 ppm  $\text{SO}_3$ . After the gas passes through the SCR reactor, its  $\text{SO}_3$  concentration increases to 5-7 ppm. The oxidation ratio of  $\text{SO}_2$  to  $\text{SO}_3$  is high (4-6%), because the catalyst was designed before low-oxidation catalysts were developed. In the air preheater, the flue gas containing about 5 ppm of  $\text{NH}_3$  is cooled to 145°C and 137°C in the No. 2 and No. 3 systems, respectively.

A substantial amount of ammonium bisulfate deposits in the air preheaters of the SCR unit. In the No. 2 system, soot blowing is applied from the cold end of the preheater using 14 kg/cm<sup>2</sup> air for 2-hour periods, 3 times a day. The pressure drop of the gas through the preheater is normally about 150 mm  $\text{H}_2\text{O}$ . After the system has been operating for three or four months, the pressure drop begins to increase rapidly. When it reaches 300 mm  $\text{H}_2\text{O}$  after about four months operation, the boiler is shut down for cleaning of the preheater. One washing requires 2,500 tons of water. The wash water containing ammonium bisulfate is stored, neutralized at a rate of 50 t/hr and stored again in preparation for reuse. One washing takes about 20 hours including the drying of the preheater. Washing is usually done on weekends when the power demand is low.

The preheaters for the No. 3 boiler have soot blowing systems at both cold and hot ends. Three times a day air blowing is applied from the cold end of the preheater; steam soot blowing from the hot end is used once a day. Even with the increased blowing, water washing is necessary only once every two or three months. Five thousand tons of water are normally used to wash both of the preheaters. Each preheater is washed while the other preheater is in use and the boiler is operating at half load.

To solve the bisulfate deposition problem in the No. 3 system, a number of measures were taken during the annual maintenance shutdown of the boiler in late 1980. First, the soot blowing system at the cold end of the preheater was modified to provide a stronger blowing action. Second, a small amount of catalyst was added to the reactor in order to reduce the unreacted  $\text{NH}_3$  from 6-8 ppm to 4-5 ppm. There was room in the catalyst container to hold the additional catalyst. Third, since dust tends to increase bisulfate deposition, the dust content of the flue gas was reduced by about one-half. The amount of dust was reduced by reducing the ratio of the flue gas recirculation and the staged combustion. This also had the effect of increasing the  $\text{NO}_x$  concentration of the flue gas from 105-110 ppm to 115-120 ppm.

So far, these modifications have proven successful with no increase in the pressure drop. The reinforced soot blowing at the cold end of the preheater is considered to be very effective; soot blowing from the hot end has been abandoned. There is no plan to add catalyst in the No. 2 system, although its soot blowing system may be reinforced in the future.

Recently Chugoku Electric, jointly with IHI, studied a new technology to remove the deposits--thermal cleaning. With this type of cleaning, the hot gas is passed through the preheater as usual while air is stopped to allow heating of the preheater elements to about  $300^\circ\text{C}$ . This causes the partial decomposition of the deposits. Intense soot blowing is applied during the heating process to dislodge the deposits. Test results have thus far not been disclosed.

#### 4.3.5 Economics

The total investment cost of the Kudamatsu SCR plant was 2.2 billion yen for the No. 2 unit and 2.5 billion yen for the No. 3 unit. These costs include civil engineering, labor, and performance testing. The No. 2 unit was relatively expensive because of the complex ductwork needed for the retrofitting process as well as the installation of the induced fans.

A breakdown of capital costs for the No. 3 SCR system is given in Table 4-9. The entire No. 3 boiler and generator system cost 55 billion yen, including 2.5 billion yen for the SCR plant and 1.2 billion yen for the ESP system. In this case the SCR system accounts for 4.5% of the total cost of the boiler-generator system.

The annual cost for the No. 3 SCR plant is given in Table 4-10. The cost assumes 70% boiler utilization or actual power generation of 4,292,400 MWhr/yr. The annualized cost for SCR adds up to 0.28 yen/kWhr (assuming a 3-year catalyst life) which is equivalent to about 1.3% of the power generation cost. This cost would increase to 0.32 yen/kWhr if the catalyst life is 2 years, and would decrease to 0.26 yen/kWhr with a 4-year catalyst life. Although a small amount of catalyst was added to the No. 3 reactor, as mentioned above, it is not certain whether the addition was really needed to reduce bisulfate deposition. A 4-year catalyst life may be attained without the addition of the catalyst.

The power consumption of the SCR system represents 0.15% of the total power generated by the boiler. This is less than one-tenth of the power consumption of conventional FGD systems. The investment cost for the No. 3 plant is 3,570 yen/kW, approximately one-fifth that of a conventional FGD system.

#### 4.3.6 Evaluation

The smooth operation of the reactor and the long life of the catalyst at Kudamatsu have demonstrated the reliability and utility of SCR for flue gas from low-sulfur oil. The ammonium bisulfate deposition problem is largely due



TABLE 4-9. CAPITAL COST BREAKDOWN OF SCR SYSTEM ON NO. 3 BOILER (700 MW)  
CHUGOKU ELECTRIC, KUDAMATSU POWER STATION (\$1 = ¥250) (3)

| Component              | Capital Cost     |                   | Percent |
|------------------------|------------------|-------------------|---------|
|                        | ¥10 <sup>9</sup> | \$10 <sup>6</sup> |         |
| Catalyst               | 1.1              | 4.4               | 44      |
| Reactor                | 0.7              | 2.8               | 28      |
| NH <sub>3</sub> System | 0.24             | 0.96              | 10      |
| Testing and Start-Up   | 0.16             | 0.64              | 6       |
| Other                  | 0.30             | 1.2               | 12      |
| TOTAL                  | 2.5              | 10.0              | 100     |

TABLE 4-10. OPERATING COST BREAKDOWN OF SCR SYSTEM ON NO. 3 BOILER (700 MW)  
CHUGOKU ELECTRIC, KUDAMATSU POWER STATION (\$1 = ¥250)

| Component       | Cost/Year        |                   | Percent |
|-----------------|------------------|-------------------|---------|
|                 | ¥10 <sup>6</sup> | \$10 <sup>6</sup> |         |
| Interest        | 250              | 1.00              | 21      |
| Depreciation    | 321              | 1.28              | 27      |
| Tax             | 35               | 0.14              | 3       |
| Catalyst        | 367              | 1.47              | 31      |
| Power           | 83               | 0.33              | 7       |
| NH <sub>3</sub> | 76               | 0.30              | 6       |
| Others          | 62               | 0.25              | 5       |
| TOTAL           | 1194             | 4.77              | 100     |

Basis: 7 years depreciation  
10% interest  
3 years catalyst life

Note: Japanese utility power company economics include the catalyst cost both in the investment cost (which is depreciated) and in the operating cost.



to the high oxidation ratio of  $\text{SO}_2$  to  $\text{SO}_3$  which occurs with certain catalysts. The new low-oxidation catalysts greatly reduce this problem.

The applicability of thermal cleaning may be related to the intensity of the soot blowing and the specific composition of the deposits. Usually, bisulfate reacts with preheater construction material to form various compounds. Combinations of some of the compounds may be difficult to remove with thermal cleaning.

#### 4.4 SCR UNIT AT THE SHIMONOSEKI PLANT, CHUGOKU ELECTRIC

##### 4.4.1 Introduction

The Shimonoseki Station of the Chugoku Electric Power Company has two boilers—a 175 MW coal-fired boiler (No. 1) and a 400 MW oil-fired boiler (No. 2). The air and water pollution regulations which apply to the station are listed in Table 4-11.

TABLE 4-11. REGULATIONS FOR SHIMONOSEKI STATION

| Pollutant                                      | Regulated Level                             |
|------------------------------------------------|---------------------------------------------|
| <u>Air Pollution Control</u>                   |                                             |
| k Value                                        | 2.7 (Ground level concentration 0.0047 ppm) |
| $\text{SO}_x$ , $\text{Nm}^3/\text{hr}$        | Below 412                                   |
| Particulates, $\text{kg}/\text{hr}$            | Below 130                                   |
| No. 1 boiler, $\text{mg}/\text{Nm}^3$          | Below 200                                   |
| No. 2 boiler, $\text{mg}/\text{Nm}^3$          | Below 40                                    |
| $\text{NO}_x$ , $\text{Nm}^3/\text{hr}$        | Below 330                                   |
| No. 1 boiler, ppm                              | Below 350                                   |
| No. 2 boiler, ppm                              | Below 170                                   |
| Suspended particulates, $\text{mg}/\text{m}^3$ | Below 0.2                                   |
| <u>Water Pollution Control</u>                 |                                             |
| pH                                             | 5.8 - 8.6                                   |
| Suspended solids, $\text{kg}/\text{day}$       | Below 12                                    |
| $\text{mg}/\text{liter}$                       | Below 15                                    |
| Normal hexane soluble material                 |                                             |
| $\text{kg}/\text{day}$                         | Below 0.8                                   |
| $\text{mg}/\text{liter}$                       | Below 1                                     |
| Chemical oxygen demand, $\text{kg}/\text{day}$ | Below 12                                    |
| $\text{mg}/\text{liter}$                       | Below 15                                    |

The No. 1 boiler was completed in 1967 and burned coal and oil at a 25/75 ratio before a full scale MHI limestone-gypsum FGD plant was completed in July 1979. After the FGD plant began operation, a 50/50 coal and oil ratio was used. Although the  $\text{NO}_x$  regulation may be met by combustion modification, even with coal as the only fuel, it is likely that more stringent  $\text{NO}_x$  reduction may be required in future. For this reason, Chugoku Electric decided to install a full-scale SCR unit to allow for the burning of coal as the sole fuel. This unit, completed in March 1980, is the first full-scale SCR plant for a coal-fired boiler in the world and is considered to be a demonstration plant.

Figure 4-12 shows the combined SCR/FGD system for the No. 1 boiler. In the system, the flue gas is first subjected to SCR at 350-400°C, then passed through two trains of air preheaters and dust collectors (multi-cyclone and ESP), and finally subjected to FGD after passing through a heat exchanger.

The No. 2 boiler is a relatively new one and uses a high sulfur oil. The boiler uses combustion modification for  $\text{NO}_x$  abatement and an MHI limestone-gypsum FGD unit to reduce  $\text{SO}_2$ .

#### 4.4.2 SCR System

The design data for the Shimonoseki SCR system are given in Table 4-12.

The No. 1 boiler is used for the station's base load and the 370°C gas temperature at its economizer outlet is suitable for SCR. The load is sometimes lowered to 25% which causes a drop in the gas temperature. Since ammonium bisulfate may deposit on the catalyst at the low temperature and thereby lower catalytic activity, an economizer by-pass system was installed (Figure 4-12). The system mixes a portion of hot gas with the economizer outlet gas at the low load in order to maintain a gas temperature of about 350°C.

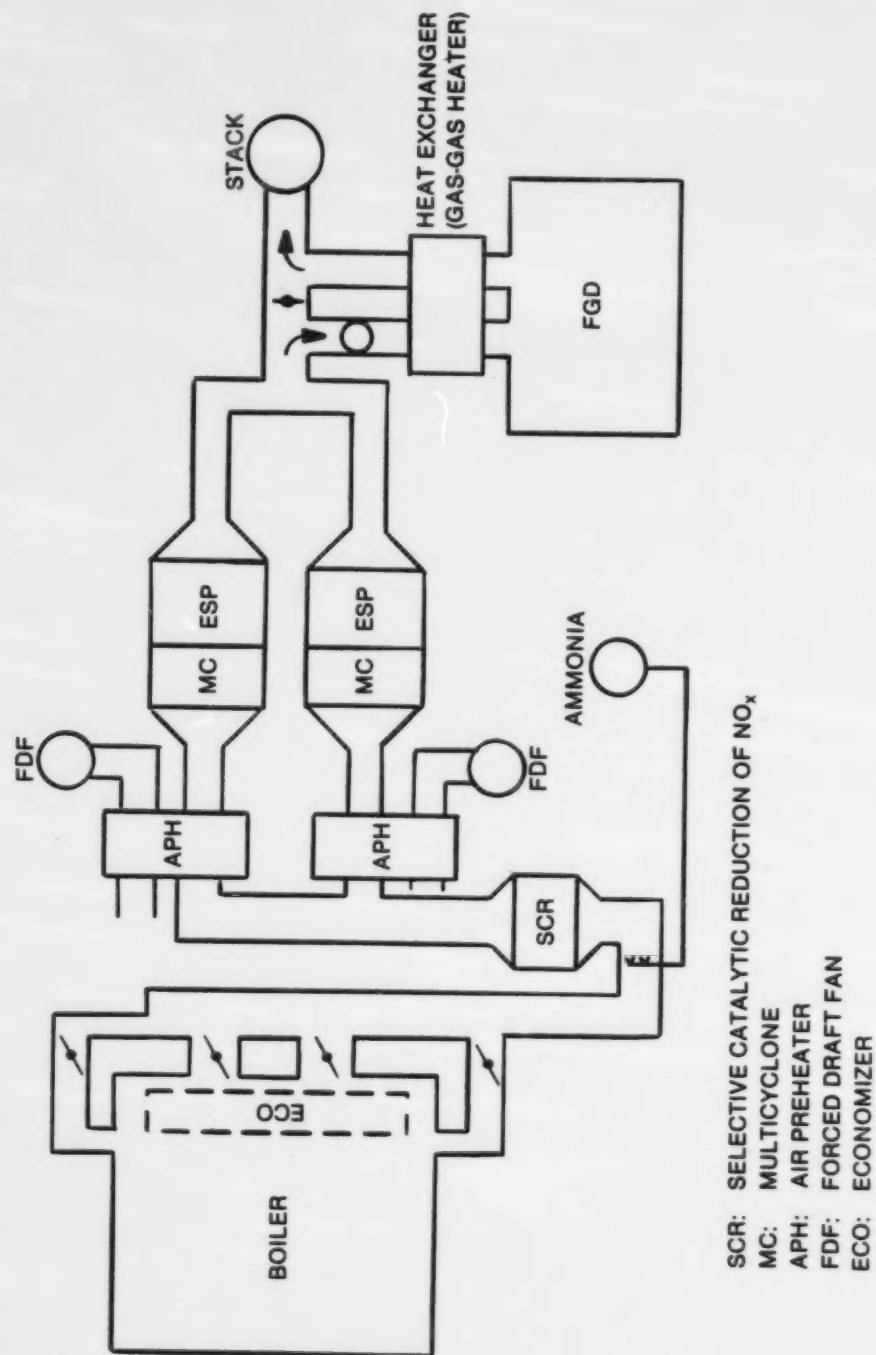


Figure 4-12 Flue Gas Treatment System for No. 1 175 MW Coal-Fired Boiler.  
 (Shimonoseki Power Station, Chugoku Electric)

TABLE 4-12. DESIGN DATA FOR THE MHI SCR SYSTEM INSTALLED AT THE SHIMONOSEKI POWER STATION

| Item                                        | Design Value                                                                         |
|---------------------------------------------|--------------------------------------------------------------------------------------|
| Flue gas flow rate                          | 550,000 Nm <sup>3</sup> /hr                                                          |
| Inlet temperature                           | 370°C                                                                                |
| Inlet NO <sub>x</sub>                       | 500 ppm                                                                              |
| NO <sub>x</sub> removal                     | 50% (Reactor sized for 80%)                                                          |
| NH <sub>3</sub> /NO <sub>x</sub> mole ratio | <0.51                                                                                |
| NH <sub>3</sub> emissions from reactor      | <10 ppm                                                                              |
| Inlet SO <sub>2</sub>                       | 1600 ppm                                                                             |
| Inlet SO <sub>3</sub>                       | 32 ppm                                                                               |
| Reactor dimensions                          | 11.8m W x 8.5m D x 13.3m H                                                           |
| Space velocity                              | 3000 hr <sup>-1</sup>                                                                |
| Catalyst                                    | Honeycomb, solid square type.<br>10 mm pitch (channel diameter plus wall thickness). |

An SCR reactor was installed adjacent to the boiler so that the treated gas could be sent to the existing air preheater (Figure 4-13). The reactor contains five horizontal layers of honeycomb catalyst (Figure 4-14) through which the gas passes downward. On top of the first honeycomb layer is a dummy layer made of inactive hard ceramic material with the same cross section as the honeycomb catalyst. This layer maintains a uniform parallel gas flow and prevents the erosion of the catalyst by fly ash. There is an open space at the bottom of the reactor where an additional catalyst layer could be placed to attain a higher NO<sub>x</sub> removal efficiency.

The planning and design of the SCR system at Shimonoseki began in July 1979; construction followed in October 1979. The boiler was modified and the reactor connected during the boiler's annual maintenance shutdown period between February and March 31, 1980. Since startup in April 1980, the boiler, SCR system, and FGD system all have been operated without problems. Normally, a 0.51-0.56 mol NH<sub>3</sub> to 1 mol NO<sub>x</sub> ratio has been used to remove 50-55% of NO<sub>x</sub>. This meets the NO<sub>x</sub> regulation and keeps unreacted NH<sub>3</sub> below 2 ppm. The system can be operated without an attendant.

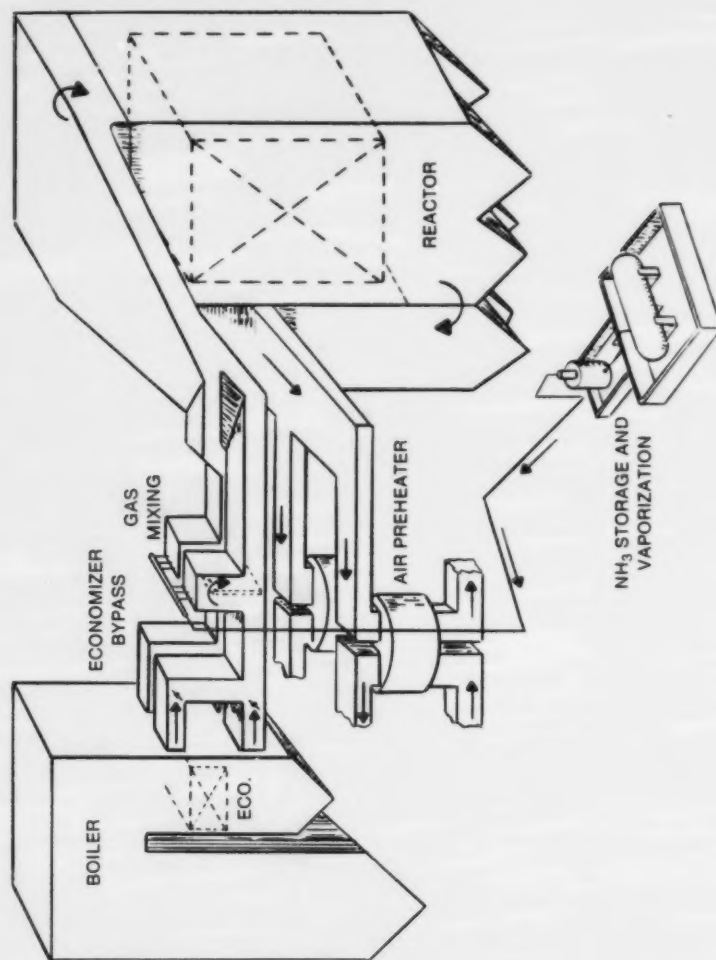


Figure 4-13 Isometric Flow Diagram of Boiler and SCR Reactor. (Shimonoseki Power Station) (3)





MHI guarantees a catalyst life of one year for its SCR system. At Shimonoseki, the catalyst was used for more than two years without any degradation, except for some very minor erosion observed at the inlet edge of the first reactor layer. Three years of catalyst life is expected and the catalyst may be replaced during the annual boiler maintenance period. The reactor has a soot blowing system but it has not been used thus far because the catalyst has remained clean.

In this system the air preheater also has been kept clean. Originally, the air preheater contained dual-undulated elements for high- and medium-temperature zones and notched flat elements for the low-temperature zone. It also was equipped with a soot blowing system at the cold end which was operated for 2-hour periods, 4 times daily. When the SCR unit was installed, a notched flat element was substituted for the dual-undulated element in the medium temperature zone: the former can be more easily cleaned by soot blowing. An additional soot blowing system was installed at the hot end of the preheater. Since the startup of the SCR system, soot blowing from both ends has been used for 2-hour periods, 4 times daily. Thus the air preheater has been kept clean and has not caused an increase in the pressure drop.

The total investment cost of the Shimonoseki SCR system was about 2 billion yen in 1980 including 1.7 billion yen paid to the builder (3).

In the future, when 80%  $\text{NO}_x$  removal is required, a small amount of catalyst will be added so that 80% removal is attained.

#### 4.4.3 Problems Related to Unreacted $\text{NH}_3$

The amount of ammonia injected in the SCR reactor at Shimonoseki is determined by the flue gas volume and inlet  $\text{NO}_x$  concentrations in a manner similar to that used at other SCR plants. The concentration of the unreacted  $\text{NH}_3$  can be measured but has not been used to determine ammonia injection because the method of measurement is less reliable than those used for other parameters. Recently the Shimonoseki station began using a new method of analyzing unreacted  $\text{NH}_3$  developed by Shimazu (Figure 4-15). A sample portion

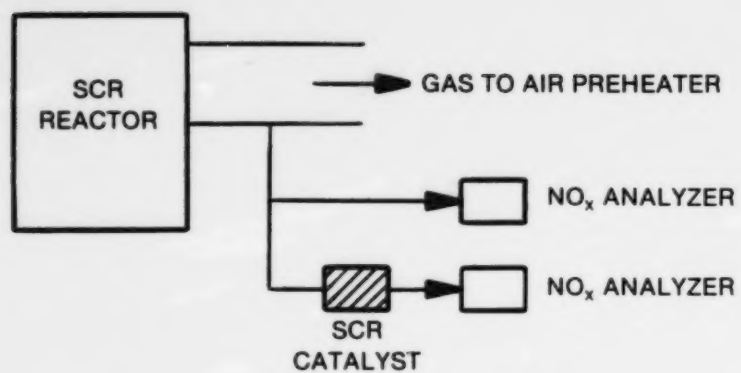


**Figure 4-15 Principle of Unreacted  $\text{NH}_3$  Analysis.**

of the reactor outlet gas is sent through the reactor (with the SCR catalyst) where all of the unreacted  $\text{NH}_3$  is converted to  $\text{N}_2$  and  $\text{H}_2\text{O}$  after reacting with the  $\text{NO}$  in the gas. The amount of  $\text{NH}_3$  in the gas is calculated by determining the difference between the  $\text{NO}_x$  concentrations in the gas which has been sent through the reactor and that which has not been exposed to the catalyst. This method seems suitable for analyzing a low level of unreacted  $\text{NH}_3$ .

The product fly ash at Shimoseki contains very little ammonia and can readily be used for cement, concrete, or landfill material. It is assumed that the ammonia contamination of the fly ash will not be extensive as long as unreacted  $\text{NH}_3$  is kept below 5 ppm.

The unreacted  $\text{NH}_3$  is eventually caught by the FGD system downstream of the air preheater. The  $\text{NH}_3$  has not caused any problems in the FGD system or with wastewater treatment because of its low concentration level.

The Shimonoseki Station's No. 2 boiler uses a high sulfur oil. For this reason, ammonia is injected into the flue gas as it leaves the air preheater in order to prevent ESP corrosion and also to increase particulate removal efficiency. Thus, the flue gas which is sent into the FGD system contains about 5 ppm  $\text{NH}_3$ , which is more than that found in the No. 1 boiler flue gas after SCR. The FGD system for the No. 2 boiler, as well as the wastewater treatment system, has had no problem with the ammonia.

#### 4.4.4 Evaluation

The smooth operation of the SCR system at Shimonoseki has demonstrated the commercial applicability of the high dust system for coal-fired boiler flue gas. The use of a dummy layer in the reactor successfully prevents catalyst erosion and is responsible for a catalyst life expectancy of more than 3 years.

The gas temperature at the SCR reactor has been kept above about  $330^\circ\text{C}$ . The critical temperature at which ammonium bisulfate deposits on the catalyst differs with the inlet  $\text{SO}_x$  concentration, the catalyst-induced oxidation

ratio of  $\text{SO}_2$  to  $\text{SO}_3$  and other factors. It has been found that with flue gas from heavy oil or crude oil, the oxidation ratio increases with time due to the deposition on the catalyst of vanadium derived from oil. This increase in oxidation may not occur with coal, particularly with the high dust system. Those problems warrant additional future study at Shimonoseki.

Since the catalyst has proved to be free from dust plugging and erosion problems, even for flue gas with a full dust load, MHI has decided to use a more efficient catalyst with a 7-mm pitch for future high-dust system SCR plants. This efficient catalyst has already been used at SCR plants for three coal-fired boilers (75 MW, 75 MW, and 125 MW) at Chugoku Electric's Shin-Ube Station, which began operation in early 1982. By using an SV of 4,000  $\text{hr}^{-1}$  and a  $\text{NH}_3/\text{NO}_x$  mole ratio of 0.66, 65% of  $\text{NO}_x$  has been removed with 2 ppm unreacted  $\text{NH}_3$ . The plants have operated successfully and the unreacted  $\text{NH}_3$  has not caused any effect on the air preheater, FGD system, or fly ash composition.

#### 4.5 SCR SYSTEM AT TOMATO-ATSUMA STATION, HOKKAIDO ELECTRIC

##### 4.5.1 Introduction

In October 1980, Hokkaido Electric completed a new 350 MW coal-fired boiler at Tomato-Atsuma. The station is located in a new industrial district developed by the Hokkaido government. The flue gas treatment system for the Tomato-Atsuma boiler is shown in Figure 4-16. In accordance with local regulations,  $\text{NO}_x$  emitted from the boiler is less than 184  $\text{Nm}^3/\text{hr}$  (158 ppm);  $\text{SO}_x$  is kept below 152  $\text{Nm}^3/\text{hr}$  (130 ppm). The boiler burns domestic low-sulfur coal containing 0.3% sulfur and 1.2% nitrogen. A hot-side ESP has been installed to maintain a high dust removal efficiency. This unit is the first hot-side ESP installed in Japan for a utility boiler. At the plant, combustion modification including staged combustion, flue gas recirculation, and a low- $\text{NO}_x$  burner, is used to reduce  $\text{NO}_x$  to 200 ppm. To meet the  $\text{NO}_x$  regulatory requirement, one-fourth of the flue gas is treated by SCR to achieve over 80%  $\text{NO}_x$  removal. A limestone-gypsum FGD system has been installed which removes over 90% of the  $\text{SO}_x$  from half of the flue gas.

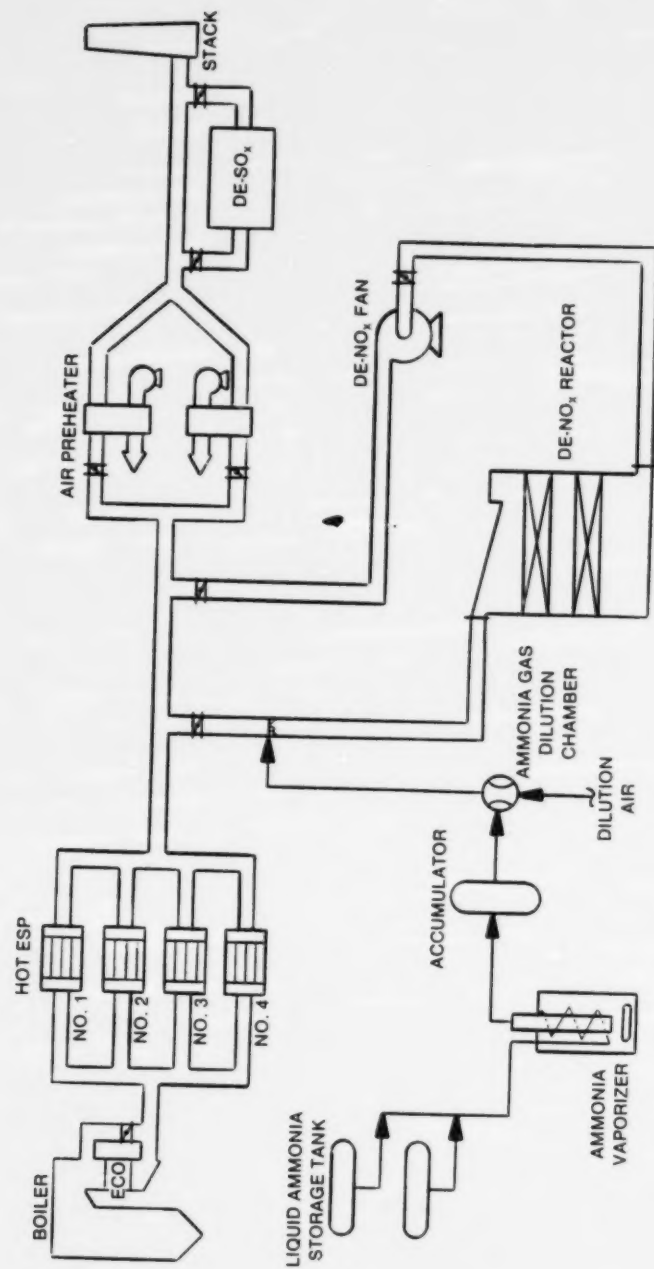


Figure 4-16 Flowsheet for the De-NO<sub>x</sub> System at the Tomato-Atsuma Station.  
(Hokkaido Electric Power Co.)



The total investment cost for the power station at Tomato-Atsuma was 70 billion yen including 11-13 billion yen for pollution control facilities. The boiler, SCR unit, and FGD unit all were constructed by Babcock Hitachi Ltd. Since its startup in October 1980, the entire system has operated smoothly, except for a few minor problems with the FGD wastewater treatment system.

#### 4.5.2 SCR System

The design conditions and equipment specifications for the Tomato Atsuma SCR unit are listed in Tables 4-13 and 4-14, respectively. A plate catalyst (1 mm thick with 10 mm pitch) produced by Hitachi Ltd. is used in the unit (Figure 4-17).

TABLE 4-13. DESIGN CONDITIONS FOR SCR UNIT, TOMATO-ATSUMA STATION, HOKKAIDO ELECTRIC POWER COMPANY

| Items                                | Design Base                 | Remarks      |
|--------------------------------------|-----------------------------|--------------|
| Gas flow                             | 280,000 Nm <sup>3</sup> /hr | 350 MW x 1/4 |
| Inlet gas temperature                | 356°C                       |              |
| Inlet NO <sub>x</sub> concentration  | Max. 200 ppm                |              |
| Outlet NO <sub>x</sub> concentration | <40 ppm                     |              |
| NO <sub>x</sub> removal efficiency   | >80%                        | (Guaranteed) |
| Inlet dust load                      | 45 mg/Nm <sup>3</sup>       |              |
| Slip ammonia concentration           | <10 ppm                     |              |
| Inlet gas humidity                   | 8.16 Vol. %                 |              |

The 360°C flue gas leaving the boiler economizer is sent through the hot-side ESP where its dust content is lowered from about 23 g/m<sup>3</sup> to 45 mg/Nm<sup>3</sup>, a removal efficiency of 99.8%. Then the gas is sent downward through an SCR reactor. Gas velocity in the reactor is about 4 m/sec. This rate is sufficient to prevent both erosion and dust plugging of the catalyst. Eighty to 85% of the NO<sub>x</sub> is removed in the reactor by using a ratio of 0.85 to 0.9 mol NH<sub>3</sub> to 1 mol NO (Table 4-15).



TABLE 4-14. PRIMARY PLANT EQUIPMENT SPECIFICATIONS

| Equipment                       | Item     | Description                             |
|---------------------------------|----------|-----------------------------------------|
| DeNO <sub>x</sub> Reactor       | Type     | Vertical Type Parallel Flow             |
|                                 | Number   | 1                                       |
|                                 | Size     | 6.6m W x 17m H x 8.8m L                 |
|                                 | Material | Carbon Steel                            |
| Catalyst                        | Type     | Plate Type (1 mm x 10 mm Pitch)         |
|                                 | Number   | Two layers                              |
|                                 | Material | Titanium base                           |
| DeNO <sub>x</sub> Fan           | Type     | Double Suction Turbo Fan                |
|                                 | Number   | 1                                       |
|                                 | Flow     | 11,900 m <sup>3</sup> /min at 356°C     |
|                                 | Pressure | -340 mmH <sub>2</sub> O (Inlet)         |
|                                 |          | -170 mmH <sub>2</sub> O (Outlet)        |
|                                 | Motor    | 480 kW, 50 Hz, 10 P                     |
| Liquid Ammonia<br>Storage Tank  | Type     | Horizontal Cylinder with Pillow Support |
|                                 | Number   | 2                                       |
|                                 | Capacity | 10 t                                    |
|                                 | Material | SB46N2SR (carbon steel)                 |
| Ammonia Vaporizer               | Type     | Vertical Spiral Tube                    |
|                                 | Number   | 1                                       |
|                                 | Capacity | Max. 113 Kg/h                           |
|                                 | Material | SS41, STPG38                            |
| Ammonia Accumulator             | Type     | Vertical Cylinder                       |
|                                 | Number   | 1                                       |
|                                 | Capacity | 0.5 m <sup>3</sup>                      |
|                                 | Material | SM41B                                   |
| Ammonia Gas<br>Dilution Chamber | Type     | Horizontal Cylinder                     |
|                                 | Number   | 1                                       |
|                                 | Material | STPG38                                  |

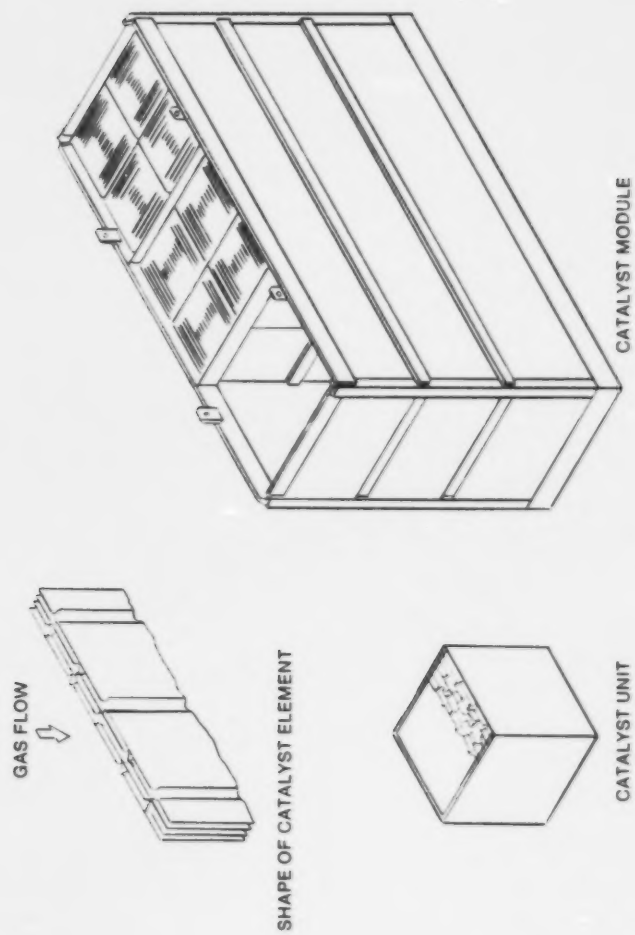


Figure 4-17 Catalyst Used in the Tomato-Aisuma SCR Unit.

TABLE 4-15. DATA, TOMATO-ATSUMA SCR UNIT, HOKKAIDO ELECTRIC POWER COMPANY

| Items                                                            | Design  | Actual  |
|------------------------------------------------------------------|---------|---------|
| Gas flow, Nm <sup>3</sup> /hr                                    | 280,000 | 287,000 |
| Inlet gas temperature, °C                                        | 356     | 332     |
| Inlet NO <sub>x</sub> concentration, ppm<br>(O <sub>2</sub> 6%)  | 200     | 181     |
| Outlet NO <sub>x</sub> concentration, ppm<br>(O <sub>2</sub> 6%) | 40      | 34      |
| NO <sub>x</sub> removal efficiency, %                            | 80      | 81.2    |
| (NH <sub>3</sub> )/(NO <sub>x</sub> ) Mole Ratio                 | 0.85    | 0.85    |
| Slip ammonia concentration, ppm                                  | 10      | 1.9     |
| Inlet gas humidity, vol %                                        | 8.16    | 10.0    |

The amount of inlet ammonia injected is determined by the inlet flue gas volume and NO<sub>x</sub> concentration. Outlet NH<sub>3</sub> concentration is sometimes measured manually; usually, the outlet NH<sub>3</sub> is kept below 5 ppm.

In May 1981, the entire system, including the boiler, was shut down for a 4-day scheduled inspection period. The SCR catalyst was found to be clean although a soot blowing system had not been installed. In addition, the air preheater had almost no deposits in it and required no cleaning. During the nearly 2-year operation period, the system did not experience any increase in the pressure drop of the preheater nor any decrease in NO<sub>x</sub> removal efficiency. Although catalyst life is guaranteed for 1 year, it is expected that the catalyst will be used for more than 2 years to maintain over 80% NO<sub>x</sub> removal efficiency with less than 10 ppm leakage NH<sub>3</sub>.

The cleanliness of the air preheater is due to the following factors:

1. Low leakage NH<sub>3</sub> in the gas (below 5 ppm) which is further diluted when the gas is mixed with untreated flue gas before entering the preheater.
2. Low SO<sub>x</sub> concentration in the gas, the low oxidation ratio of SO<sub>2</sub> to SO<sub>3</sub> (about 0.2%) caused by the catalyst, and the dilution by untreated flue gas.

3. Low dust content of the gas.

4. The use of soot blowing.

#### 4.5.3 Future Construction

In 1985, Hokkaido Electric will complete the construction of a 600-MW coal-fired boiler at the Tomato-Atsuma station. This No. 2 boiler will be constructed by IHI; Hitachi Ltd will supply the turbines. Imported coal, containing 1.2% S and 1.8% N, will be used with extensive combustion modification to maintain  $\text{NO}_x$  below 170 ppm. This combination will enable the boiler to comply with the regulations without requiring SCR. The flue gas leaving the air preheater will be treated by a cold ESP and an MHI limestone-gypsum FGD system. Although the No. 2 boiler will not have an SCR reactor, a space between the boiler economizer and air preheater will be reserved for future installation of a high-dust SCR system.

#### 4.5.4 Evaluation

The SCR unit at Tomato-Atsuma is the first commercial low-dust SCR unit to use a hot ESP for flue gas from coal. The smooth operation of the plant demonstrates that the low-dust system, as well as the high-dust system, is feasible. The Hitachi plate catalyst is very efficient and removes over 80% of  $\text{NO}_x$  with only a small amount of unreacted  $\text{NH}_3$ .

Several years ago when Hokkaido Electric decided to use the low-dust system, the high-dust system had not yet proved to be viable; now Hokkaido Electric is interested in using the high-dust system. Although the company currently has no plans to install an SCR system for the No. 2 boiler, a high-dust system will be installed if SCR proves to be necessary.

#### 4.6 KANSAI ELECTRIC'S SCR PLANTS

##### 4.6.1 Large Scale Testing of SCR

Kansai Electric, the second largest utility company in Japan, first installed an SCR test plant in 1977. The plant is capable of treating one-fourth of the flue gas from an existing 450 MW oil-fired boiler at the Kainan Station. Initially, a ring tube catalyst was used in a fixed bed. The flue gas contains about 100 ppm each of  $\text{SO}_x$  and  $\text{NO}_x$  with about 20 mg/ $\text{Nm}^3$  of particulates. The 330-380°C flue gas leaving the boiler economizer enters the SCR reactor where over 80% of  $\text{NO}_x$  is removed and unreacted  $\text{NH}_3$  is maintained at around 10 ppm. At first, the reactor had dust plugging problems and as a result, the ring tube catalyst was replaced by a Hitachi plate catalyst. With the new catalyst, the SCR system has experienced trouble-free operation.

In 1977, Kansai Electric also installed a Thermal De $\text{NO}_x$  SNR system for an existing 156 MW boiler at its Himeji Station. In 1978, a small amount of a honeycomb SCR catalyst was installed in the duct between the boiler economizer and the air preheater in order to increase  $\text{NO}_x$  removal efficiency and reduce unreacted  $\text{NH}_3$ . The SNR unit was removed in 1979. Since then, about 30% of the  $\text{NO}_x$  has been removed by the catalyst and a small amount of ammonia has been injected between the boiler economizer and the catalyst bed.

Both of the plate catalysts at Kainan and the honeycomb catalyst at Himeji have been used with little degradation for about 4 years. Based on these results, Kansai Electric has installed many commercial SCR plants which use honeycomb and plate catalysts (Table 4-1).

##### 4.6.2 Commercial SCR Plants

As shown in Table 4-1, Kansai Electric has 25 commercial SCR plants for existing oil- and gas-fired boilers and plans to install 6 plants for new oil-fired boilers. Twenty-one plants which use honeycomb catalysts have been or will be constructed by MHI and IHI; Babcock Hitachi has or will construct

another 10 plants which use plate catalysts. All of the SCR reactors are placed between the boiler economizer and air preheater.

As shown in Figure 4-18, the SCR reactors for the Sakaiko Station's No. 2, 4, 6 and 7 boilers (250 MW each) are each placed in a small space at the economizer outlet. The reactors use MHI honeycomb catalysts with a space velocity of  $5,070 \text{ hr}^{-1}$  so that flue gases from both oil and gas burning can be treated.

The SCR system performance for the No. 6 boiler which fires LNG is shown in Figure 4-19. The flue gas contains about 110 ppm  $\text{NO}_x$ . By using 0.8 mol  $\text{NH}_3$  per mol of  $\text{NO}_x$ , over 75 percent of the  $\text{NO}_x$  is removed with less than 5 ppm of unreacted  $\text{NH}_3$ . During 13,000 hours of operation, the SCR system showed only a slight decrease in  $\text{NO}_x$  removal efficiency--from 77-78% at the beginning to 76-77% at the end.

Figure 4-20 shows the retrofitting of the SCR reactor for the existing No. 2 boiler (156 MW) at Kansai Electric's Osaka Station. The SCR reactor is positioned just above the vertical flow preheater so that the gas is sent downward through the reactor. SCR reactors also have been installed for the Nos. 3 and 4 boilers. These boilers burn 1% sulfur oil and produce flue gas containing about 500 ppm  $\text{SO}_2$  with a small amount of  $\text{SO}_3$ . To meet regulatory requirements, a low oxidation honeycomb catalyst is used to remove 75% of  $\text{NO}_x$  and to maintain unreacted  $\text{NH}_3$  below 5 ppm.

As of July 1982, the SCR systems for boiler Nos. 2 and 4 have operated without problems for about 9,000 hours. There has been no ammonium bisulfate deposition in the air preheaters, which may be due to the low levels of unreacted  $\text{NH}_3$  and  $\text{SO}_3$ .

Osaka Station's No. 1 oil-fired boiler (156 MW) has a simple SCR system which uses a small amount of catalyst in the duct between the boiler economizer and air preheater. This system removes about 30% of  $\text{NO}_x$ .



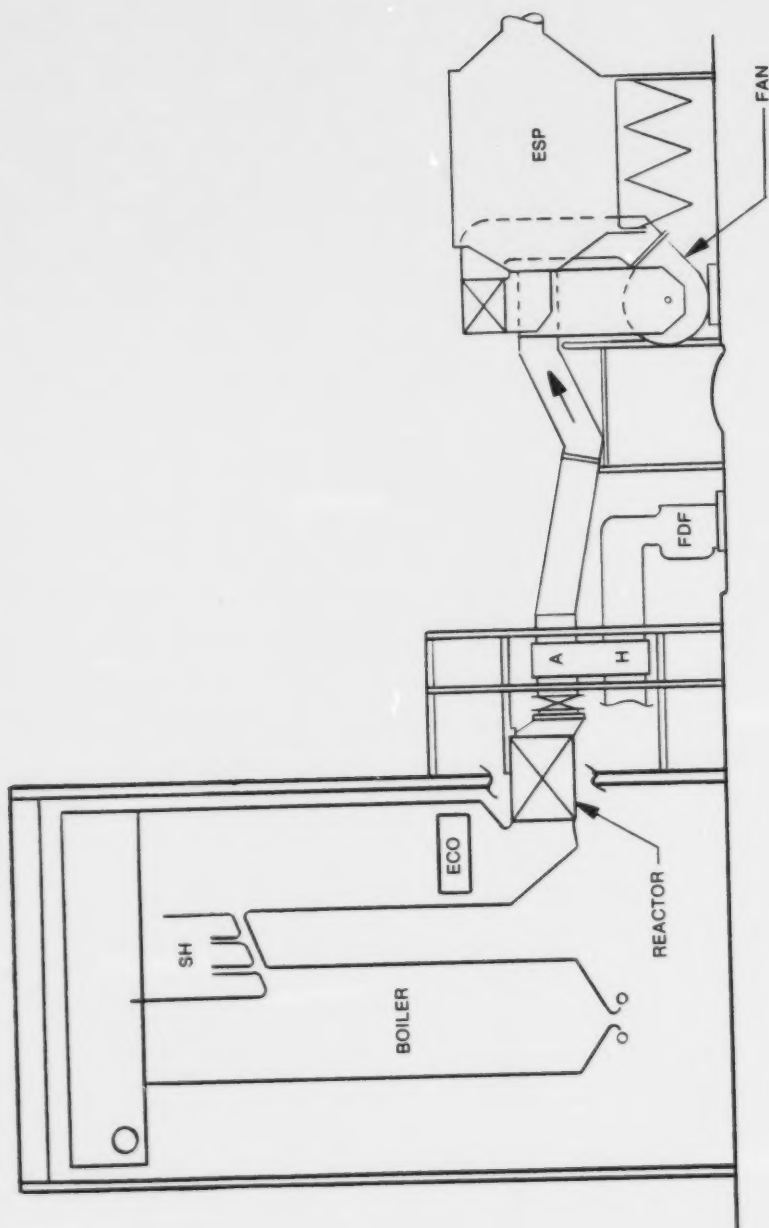
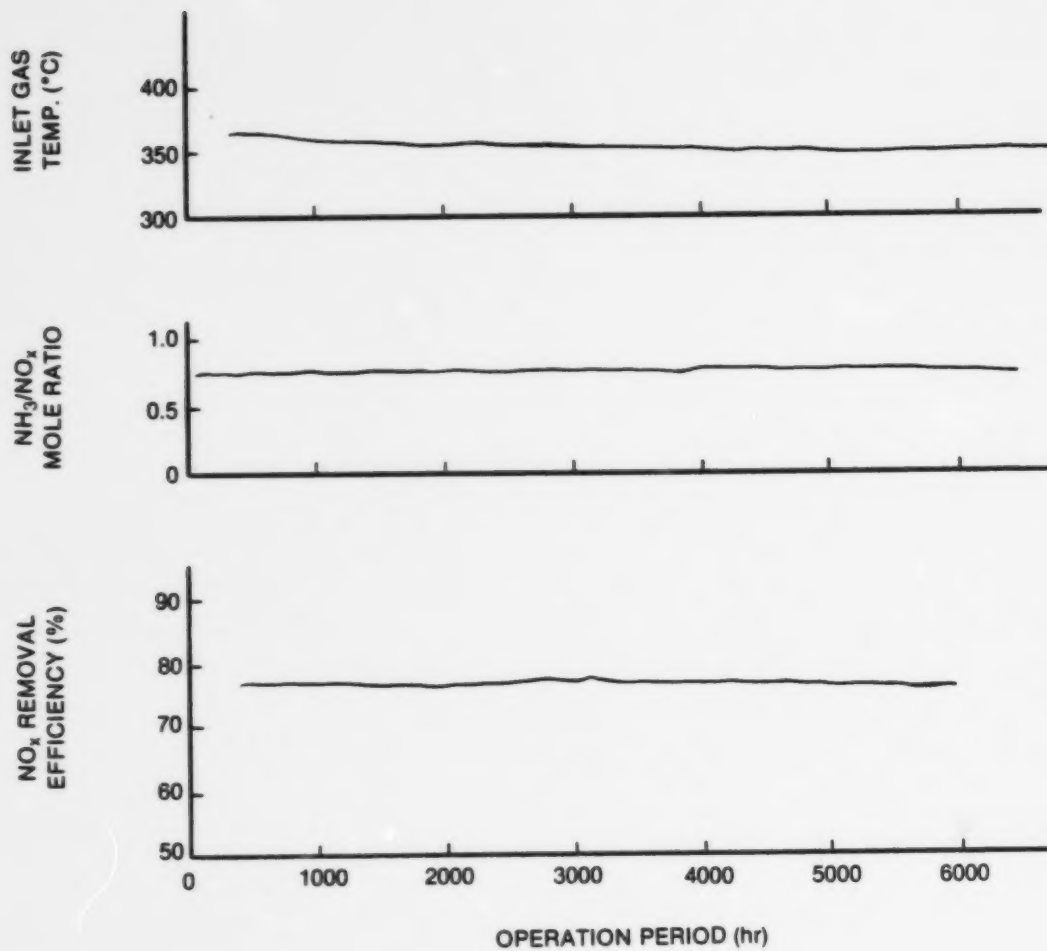


Figure 4-18 SCR Reactor Retrofitted to Boiler Nos. 2, 4, 6, and 7.  
(Sakai Electric Power Company)



(Figures plot data once a day at full load)

**Figure 4-19** Performance of the SCR Unit for the 250 MW, LNG-Fired No. 6 Boiler.  
(Sakaiko Station)

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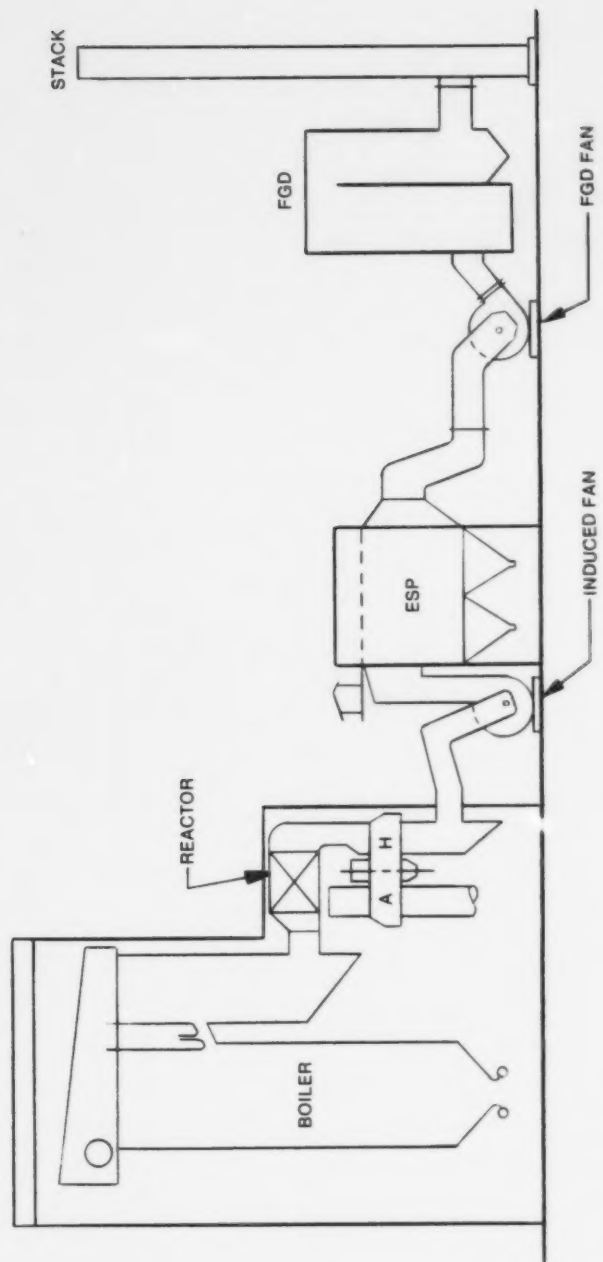


Figure 4-20 SCR Reactor Retrofitted to Boiler Nos. 2, 3, and 4.  
(Osaka Station, Kansai Electric Power Company)

Figure 4-21 shows the SCR reactor which was retrofitted to the existing No. 6 boiler (600 MW) at Kansai's Himeji No. 2 Station. The boiler burns either oil or gas. IHI constructed the SCR plant which uses a honeycomb catalyst; a large additional amount of ductwork was required to connect a large reactor between the boiler economizer and air preheater. The boiler has two trains of air preheater-ESP systems and therefore required an SCR reactor for each of the trains. The boiler burns LNG currently and the SCR systems have been operated without problems.

#### 4.6.3 Evaluation

Kansai Electric's SCR units have been operated without problems. The lack of a bisulfate deposition problem in the unit's air preheaters may be due to the use of a catalyst with a low  $\text{SO}_2$  oxidation capability and to a low level of unreacted  $\text{NH}_3$ .

### 4.7 SCR TESTS AT THE NAKOSO STATION (5)

#### 4.7.1 Test Plant

Tokyo Electric Power Company, Tohoku Electric Power Company, Joban Joint Power Company, and MHI conducted extensive testing of SCR with flue gas (4,000  $\text{Nm}^3/\text{hr}$ ) from the No. 7 boiler at Joban's Nakoso Station. The tests were run from April 1979 to November 1980. The No. 7 boiler burned 40% coal and 60% oil in the daytime and 60-70% coal/30-40% oil during the reduced load period at night.

The flowsheet of the test plant is shown in Figure 4-22. The plant consisted of both high-dust and low-dust SCR systems in combination with wet limestone-gypsum FGD system. The high-dust system treated flue gas with a full dust load of 6-10  $\text{g}/\text{Nm}^3$ . It used 2 downflow SCR reactors with honeycomb or plate catalysts. In the high-dust system, a ceramic dummy spacer was placed above the catalyst layer to protect the catalyst from fly ash erosion. In the low-dust system, the flue gas first was sent through a hot ESP where the dust content was reduced to 0.1-0.3  $\text{gram}/\text{Nm}^3$ . From there, the gas went

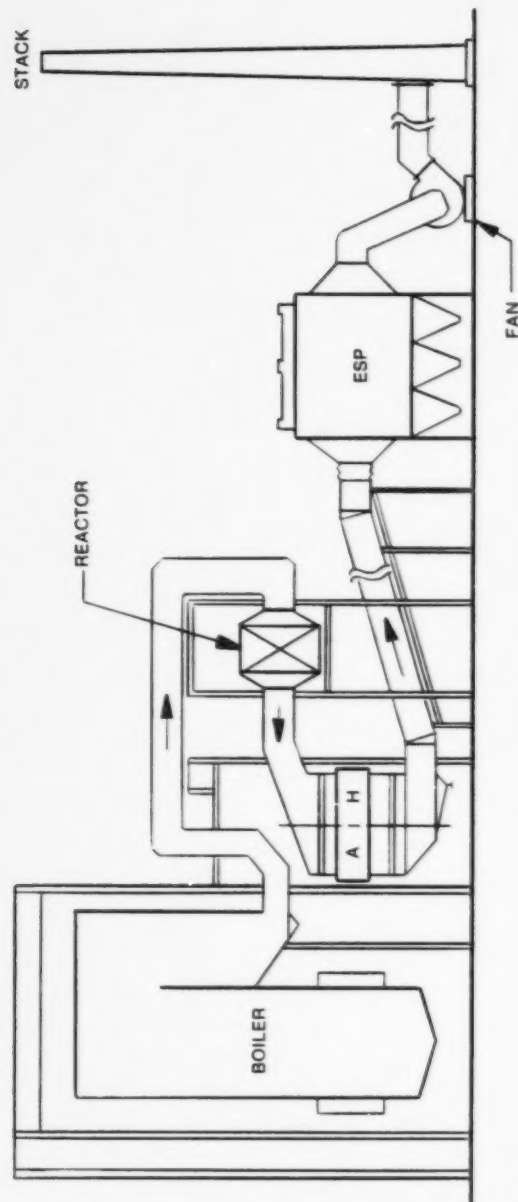


Figure 4-21 SCR Reactor Retrofitted to Boiler No. 6. (Himeji Station, Kansai Electric Power Company)





into 3 SCR reactors in parallel. Two of the reactors used either a honeycomb or plate catalyst with horizontal gas flow while the third used a honeycomb catalyst with gas downflow. A vertical flow air preheater was installed downstream of each of the reactors.

#### 4.7.2 Test Results

Tests were conducted for a total of 10,600 hours, excluding monthly shutdown periods for inspection. These shutdown periods typically lasted several days.

Figure 4-23 summarizes 1979 test results for the high-dust system. An  $\text{NO}_x$  removal efficiency of 80% was attained throughout the test period. The catalysts were kept clean and showed no degradation; the dummy layer successfully prevented catalyst erosion.

During the test period the pressure drop of the gas through the catalyst bed remained at about 25 and 15 mm  $\text{H}_2\text{O}$  for the main and sub reactors, respectively, without soot blowing.

The air preheater contained dual-undulated elements for high- and intermediate-temperature zones and a notched flat element for the low-temperature zone. Soot blowing was applied once a day to keep the preheater clean. There was no increase in the pressure drop through the preheater during the entire 10,600 hour test period. Unreacted  $\text{NH}_3$  was maintained at 1-3 ppm. Results of the first 5,000 hours of testing are given in Figure 4-24.

Figures 4-25 and 4-26 present results of tests on the low-dust system. Without soot blowing, fine particles of fly ash deposited horizontally on the inlet edge of the honeycomb catalyst. This caused an increase in the pressure drop and a decrease in the  $\text{NO}_x$  removal efficiency. The ash deposits were removed by soot blowing. Deposition can be reduced by using a honeycomb with a larger channel diameter or with a higher gas velocity, but these measures will not prevent the large increase in the pressure drop which occurs when

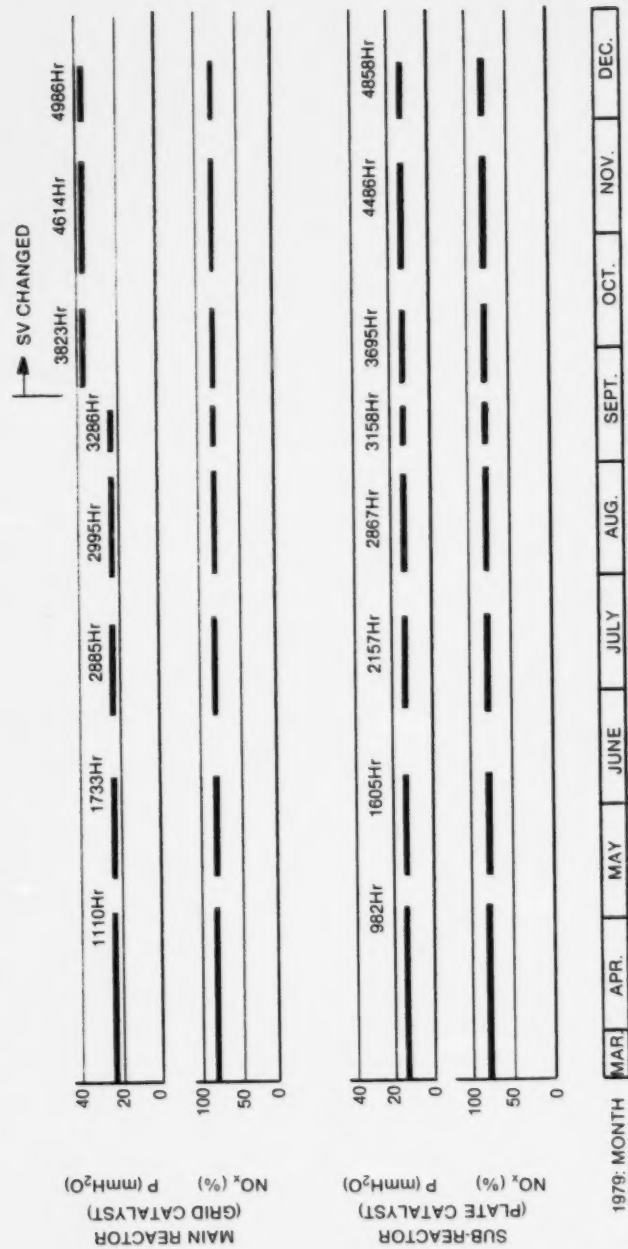


Figure 4-23 Operating Experience of High-Dust De-NO<sub>x</sub> System.



SB: SOOT BLOWING  
NOT USED EXCEPT WHERE NOTED

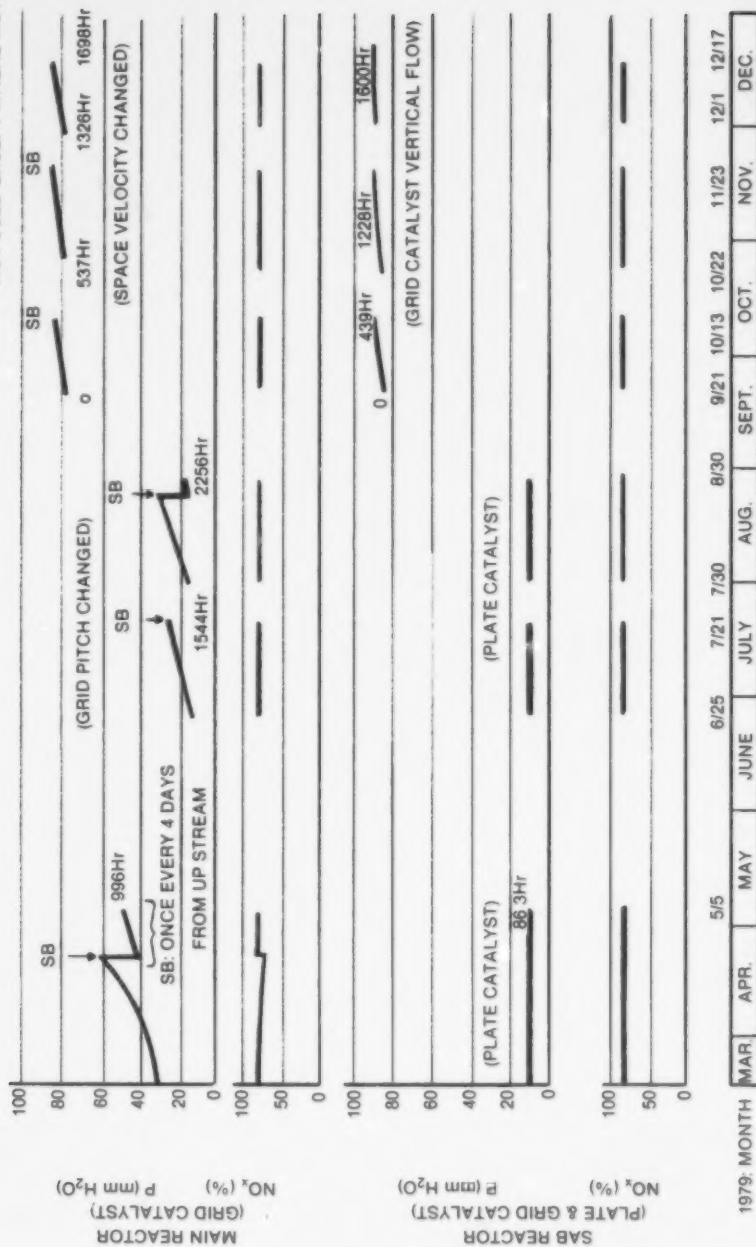


Figure 4-25 Operating Experience of Low-Dust De-NO<sub>x</sub> System.

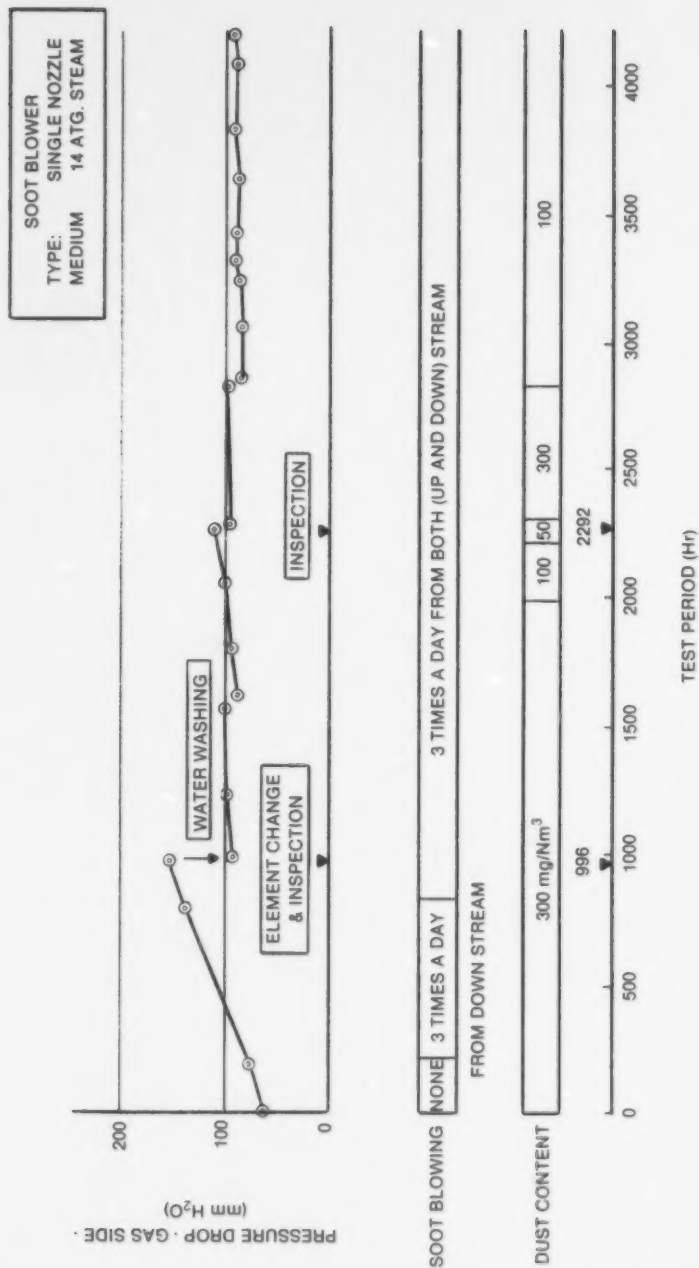


Figure 4-26 Operating Experience of Air Preheater vs. Soot Blowing (low dust content)

soot blowing is not used. About 80%  $\text{NO}_x$  removal efficiency and unreacted  $\text{NH}_3$  in the range of 1-3 ppm was achieved throughout the test period.

The air preheater experienced ammonium bisulfate problems when it contained the standard types of elements. As shown in Figure 4-26, the pressure drop increased markedly even with soot blowing three times a day. After 996 hours of operation, the preheater was washed with water and the elements in the intermediate- and low-temperature zones were replaced with new notched-flat elements which permit soot blowing to work more efficiently. After the change of elements, any increase in pressure drop was prevented by applying soot blowing three times a day from both cold and hot sides of the preheater.

#### 4.7.3 Evaluation

Based on these tests, Tokyo Electric considers both the high-dust and low-dust SCR systems to be commercially applicable to coal-fired boilers, the high dust being superior to the low-dust. Two commercial SCR plants under construction for the Nos. 8 and 9 coal/oil-fired boilers at the Nakoso Station (600 MW each) will use the high-dust system.

However, the high-dust system does have two problems associated with it (1) contamination of fly ash by ammonia, and (2) a relatively low cold ESP efficiency for fly ash from low-sulfur coal. As the tests have demonstrated, contamination of the fly ash can be eliminated by maintaining unreacted  $\text{NH}_3$  at a very low level. The problem of the low ESP efficiency can be solved by applying wet process FGD which is very effective at removing particulates. The tests at Nakoso showed that a particulate concentration of  $300 \text{ mg/Nm}^3$  can be reduced to about  $30 \text{ mg/Nm}^3$  by FGD (5).



#### 4.8 EPDC'S SCR ACTIVITIES (6)

##### 4.8.1 Introduction

In cooperation with five major SCR process developers, EPDC conducted extensive pilot plant tests of both high- and low-dust SCR systems with coal-fired flue gas. For the full-scale demonstration plant (250 MW) and for a commercial plant for a new 700-MW coal-fired boiler, EPDC tested the low-dust system. This section was made in order to maintain a low dust emission level with various types of imported coals and to eliminate ammonia contamination of the fly ash.

##### 4.8.2 Pilot Plant Tests with KHI (7)

Figure 4-27 is the flowsheet of the Takehara SCR pilot plant. In the plant, the 150°C flue gas leaving the existing ESP is heated by a heat exchanger and electric heater to 300°-400°C. The composition of the flue gas and the properties of the fly ash are shown in Table 4-16. The composition of the fly ash is shown in Table 4-17.

TABLE 4-16. FLUE GAS COMPOSITION AND FLY ASH PROPERTIES, SCR PILOT PLANT, TAKEHARA STATION

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|                                    |                             |
|------------------------------------|-----------------------------|
| Flue gas contents:                 |                             |
| NO <sub>x</sub> , ppm              | 200 ~ 410                   |
| SO <sub>2</sub> <sup>x</sup> , ppm | 1100 ~ 1720                 |
| SO <sub>3</sub> , ppm              | 1 ~ 2                       |
| O <sub>2</sub> , %                 | 5 ~ 10 %                    |
| H <sub>2</sub> O, %                | 8 ~ 9 %                     |
| Dust, mg/Nm <sup>3</sup>           | 46 ~ 255 mg/Nm <sup>3</sup> |
| Dust properties:                   |                             |
| Particle size, μ                   | 10 ~ 30μ                    |
| Specific gravity                   | ca. 2.1 (absolute)          |

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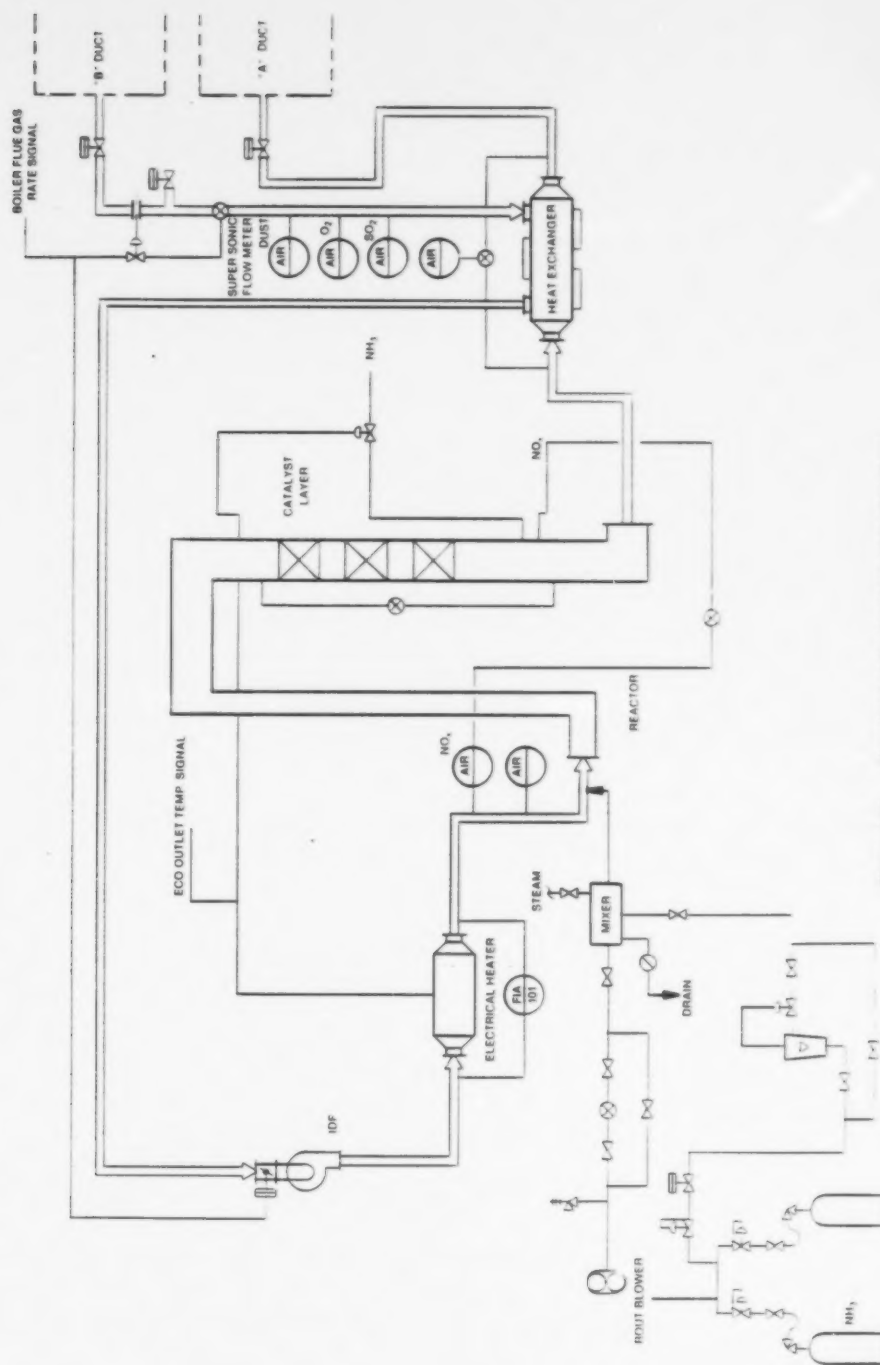


Figure 4.27 Flowsheet of the Takehara SCR Pilot Plant.

TABLE 4-17. FLY ASH COMPOSITION.

|                   |                                |                                |                                |                                |                               |
|-------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|
| SiO <sub>2</sub>  | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO                            | MgO                            | V <sub>2</sub> O <sub>5</sub> |
| 56.91             | 4.92                           | 21.5                           | 1.57                           | 1.28                           | 0.04                          |
| Na <sub>2</sub> O | K <sub>2</sub> O               | PbO                            | MnO                            | TiO <sub>2</sub>               | CuO                           |
| 0.57              | 0.22                           | 0.03                           | 0.04                           | 1.67                           | 0.01                          |
| ZnO               | NH <sub>4</sub> <sup>+</sup>   | Cl <sup>-</sup>                | SO <sub>4</sub> <sup>---</sup> | CO <sub>3</sub> <sup>---</sup> | C                             |
| 0.02              | <0.01                          | Nil                            | 0.77                           | 0.44                           | 3.5                           |

The pilot plant uses a vertical SCR reactor with a gas down flow and a tubular catalyst. The objective of the pilot plant test was to attain 80% NO<sub>x</sub> removal efficiency with unreacted NH<sub>3</sub> less than 5 ppm. The SO<sub>2</sub> oxidation ratio caused by the catalyst was about 1%.

Figure 4-28 shows the relationship between the gas velocity in the reactor (linear velocity), space velocity, gas temperature, and NO<sub>x</sub> removal efficiency. Over 90% of NO<sub>x</sub> was removed at temperatures above 350°C with an SV of 4,160 hr<sup>-1</sup> or less and an NH<sub>3</sub>/NO<sub>x</sub> mole ratio of 1.0, although a considerable amount of unreacted NH<sub>3</sub> was released.

Figure 4-29 shows that by using a mole ratio of 1.0 at the SV of 3,120 hr<sup>-1</sup>, unreacted NH<sub>3</sub> exceeded 5 ppm, although the NO<sub>x</sub> removal efficiency exceeds 90%. In order to keep the level of unreacted NH<sub>3</sub> below 5 ppm, the mole ratio should be smaller than 0.9, which will result in an NO<sub>x</sub> removal efficiency below 90%. An SV smaller than 3,000 hr<sup>-1</sup> may be used in large-scale SCR units to achieve the same results. Figure 4-30 shows that catalytic activity did not decrease during the 4,000 hour test period. Nor did the pressure drop, which indicates that no dust plugging occurred.

Figures 4-31 and 4-32 illustrate the results of special tests using one-third the normal amount of catalyst. In one of the tests, the gas temperature was varied between 360° and 290°C with a temperature change rate of 3.3°C/min. for the descending rate and 3.1°C/min. for the ascending rate (Figure 4-32).

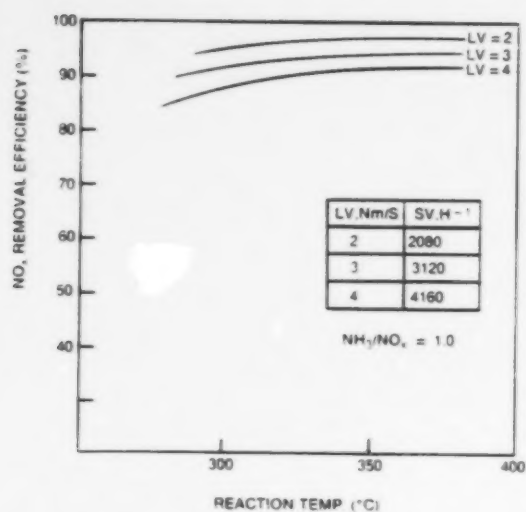


Figure 4-28 Effect of Reaction Temperature on NO<sub>x</sub> Removal Efficiency. SCR Pilot Plant, Takehara Station.

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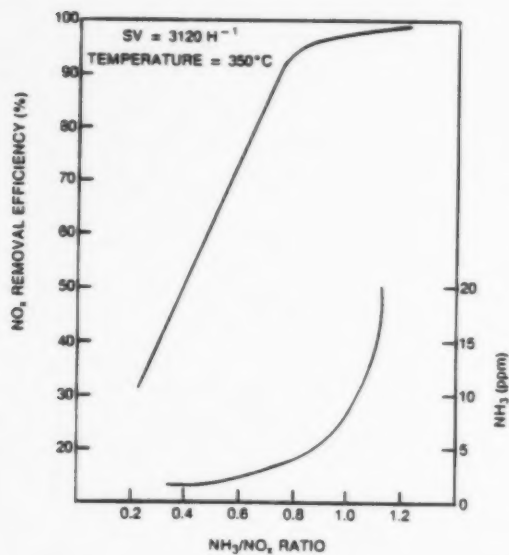


Figure 4-29 Effect of NH<sub>3</sub>/NO<sub>x</sub> Ratio on NO<sub>x</sub> Removal Efficiency and Unreacted NH<sub>3</sub>, SCR Pilot Plant, Takehara Station.

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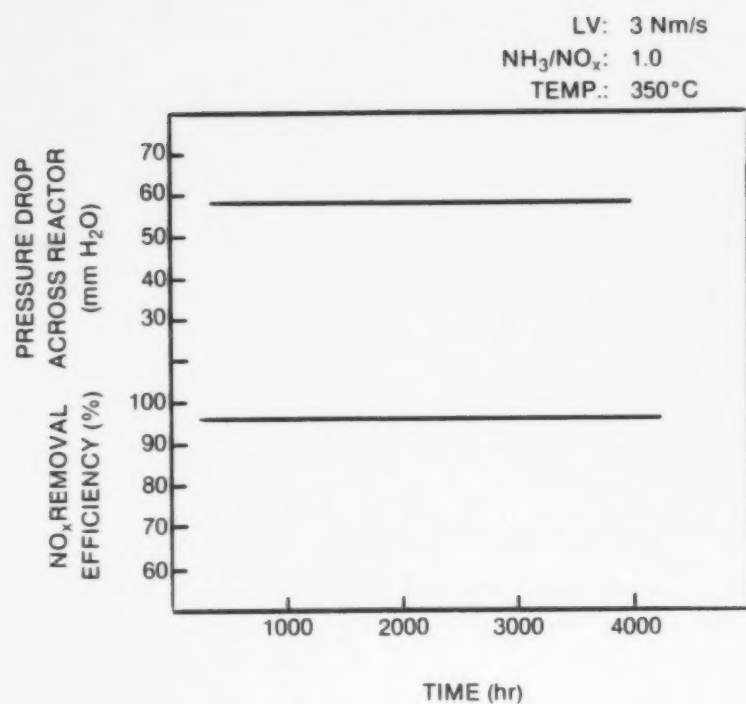


**Figure 4-30** NO<sub>x</sub> Removal Efficiency and Pressure Drop During 4000 hr Test Period, SCR Pilot Plant, Takehara Station.

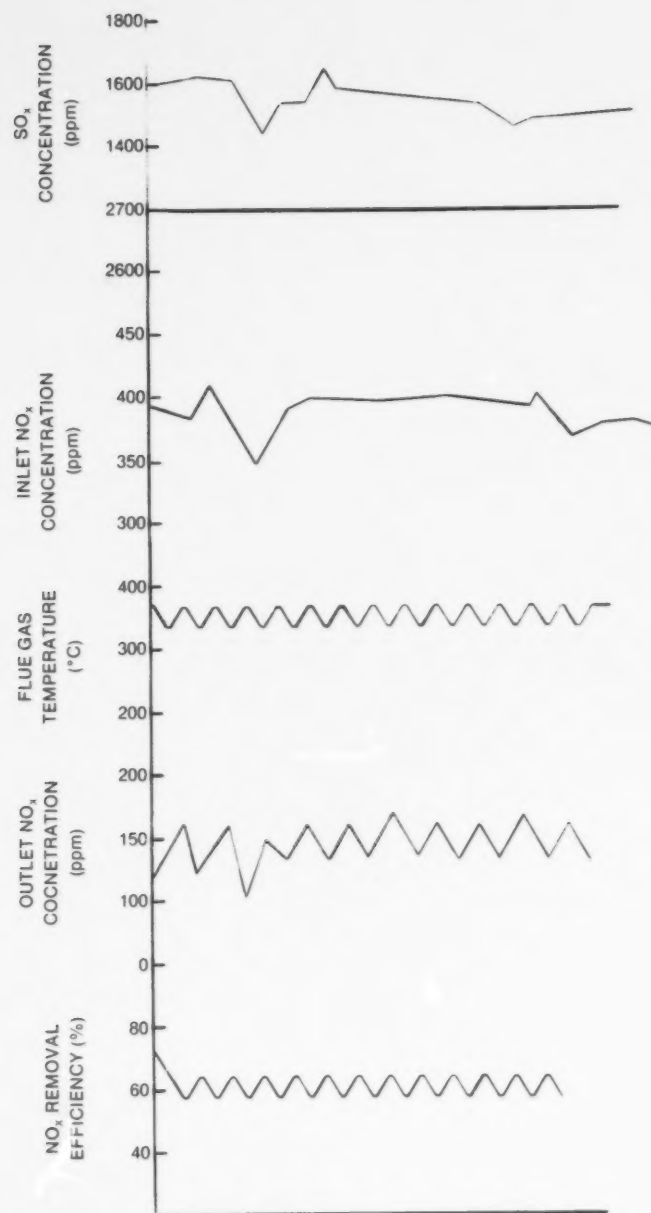


Figure 4-31 Temperature Swing Test Results, SCR Pilot Plant, Takehara Station.



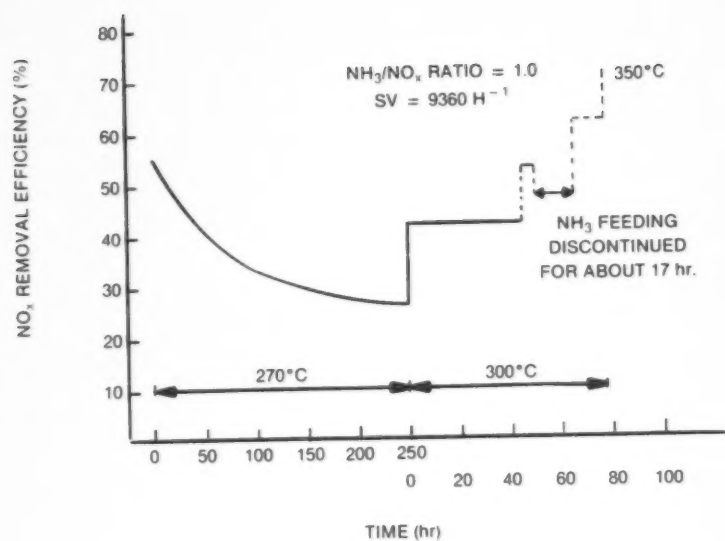


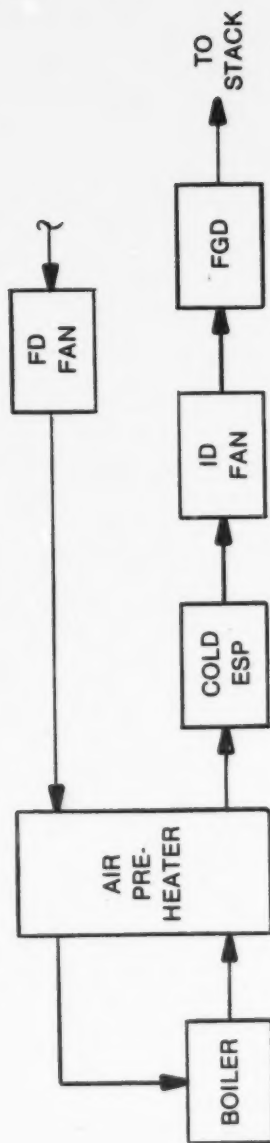
Figure 4-32 NH<sub>3</sub> Injection at Low Temperature and Recovery Test, SCR Pilot Plant, Takehara Station.

No change in the  $\text{NO}_x$  removal efficiency was observed before or after the test. Figure 4-33 shows that the  $\text{NO}_x$  removal efficiency decreased from 60% to about 30% when the gas temperature was maintained at  $270^\circ\text{C}$  for 250 hours due to ammonium bisulfate deposition on the catalyst. When the gas temperature was raised to  $300^\circ\text{C}$ , the  $\text{NO}_x$  removal efficiency increased to over 40%. When the gas was heated even more ( $350^\circ\text{C}$ ), catalytic activity returned to its initial level. These results indicate that the catalyst was resistant to attack by the ammonium bisulfate.

#### 4.8.3 Demonstration Plant

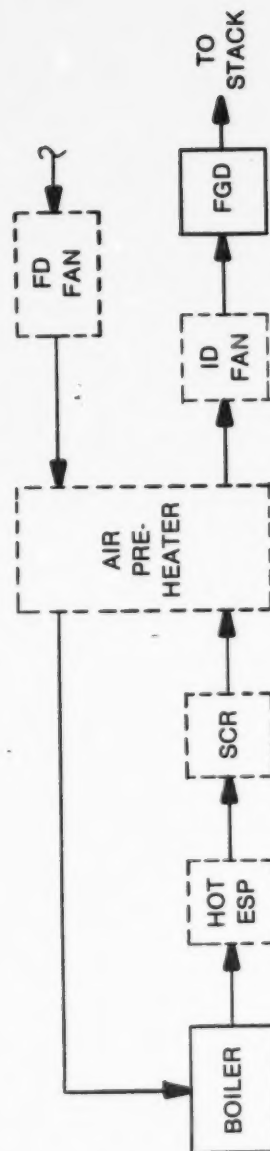
Basic information on the SCR demonstration plant at the Takehara Station is presented in Table 4-18 and Figures 4-33 and 4-34. The No. 1 coal-fired boiler (250 MW) has two trains of air preheater/cold ESP/ ID fans. After passing through this system, all of the boiler flue gas is treated by wet limestone/gypsum FGD. For the demonstration test, a system with two trains of hot ESP/SCR/fans and modified air preheaters was installed. One of the SCR reactors is manufactured by BHK and uses a plate catalyst similar to the one used at Hokkaido Electric's Tomato-Atsuma Station (Section 4.5) with an SV of  $2,300 \text{ hr}^{-1}$ ; the other is manufactured by KHI and uses a tubular catalyst with an SV of about  $2,000 \text{ hr}^{-1}$ .

The air preheater used in the demonstration has a modified arrangement of elements and soot blowers as shown in Figure 4-35. Ammonium bisulfate tends to deposit between the intermediate- and low-temperature zones in a conventional air preheater and is difficult to remove by conventional soot blowing. To solve that problem a combined intermediate- and low-temperature element was installed which permits soot blowing to work efficiently. The new fans installed in the SCR demonstration plant are compared with the existing ones in Table 4-19. The increase in the capacity of the induced fans is designed to compensate for the increase in the pressure drop caused by SCR reactor and hot ESP. An increased capacity in the forced draft fans is required by the large distance between the fan and the boiler caused by the retrofitting of the SCR system.



EXISTING ARRANGEMENT

— EXISTING  
 - - - NEW



MODIFIED ARRANGEMENT

Figure 4-33 Equipment Modifications Made for SCR System Installation at EPDC's Takehara Station. (8)

TABLE 4-18. DESCRIPTION OF SCR DEMONSTRATION PLANT, TAKEHARA STATION NO. 1 UNIT

| Item                                                | Manufacturer | Type                             | Capacity                                                 | Efficiency<br>(Guaranteed) | Remarks              |
|-----------------------------------------------------|--------------|----------------------------------|----------------------------------------------------------|----------------------------|----------------------|
| (1) Existing Plant                                  |              |                                  |                                                          |                            |                      |
| (a) Boiler                                          | BHK          | Reheat Type<br>Radiant<br>Boiler | 810 T/h                                                  | -                          | Fuel: coal           |
| (b) Plant output                                    | -            | -                                | 250 MW                                                   | -                          |                      |
| (2) Demonstration Plant                             |              |                                  |                                                          |                            |                      |
| (a) SCR                                             | BHK<br>KII   | Plate Catalyst<br>Tube Catalyst  | 400,000 Nm <sup>3</sup> /h<br>400,000 Nm <sup>3</sup> /h | >80%<br>>80%               |                      |
| (b) Air Preheater                                   | Gadiluis     | Long element<br>Ljungstrom       | 400,000 Nm <sup>3</sup> /h<br>x 2                        | -                          | New Air<br>Preheater |
| (c) NH <sub>3</sub> Removal<br>from FGD<br>Blowdown | IZ           | Activated<br>Sludge              | 1,000 m <sup>3</sup> /Day                                | <10 ppm<br>as total N      |                      |

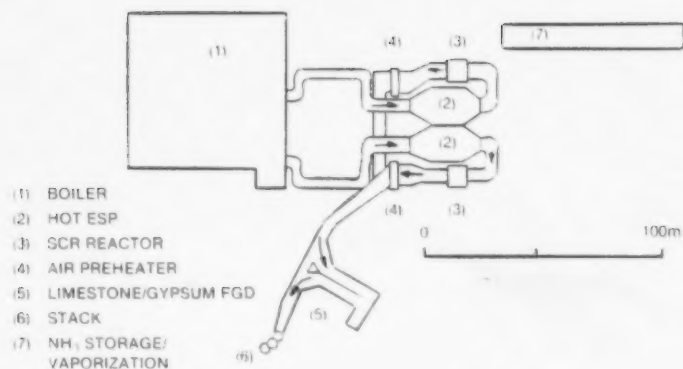


Figure 3-34 Arrangement of the SCR Demonstration Plant, Takehara Station, EPDC. (3)

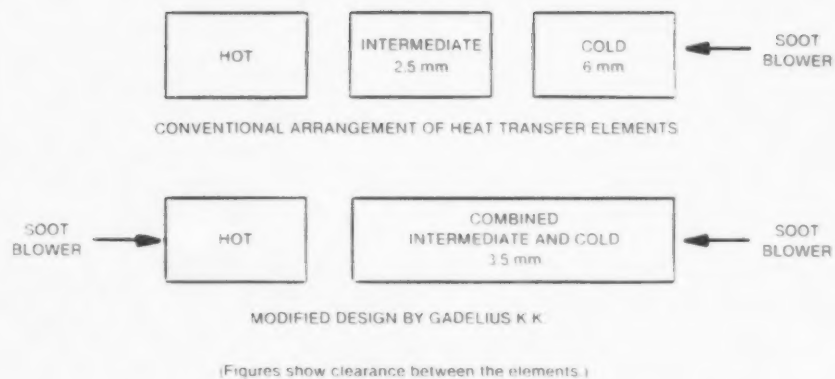


Figure 4-35 Conventional and Modified Air Preheater Designs. (9)

TABLE 4-19. COMPARISON OF EXISTING AND NEW FANS AT TAKEHARA POWER STATION (KW)

| Fan                      | Existing | New      |
|--------------------------|----------|----------|
| Forced Draft (air)       | 630 x 2  | 1350 x 2 |
| Induced Draft (flue gas) | 1350 x 2 | 2350 x 2 |

The Takehara SCR units began operation in 1981 and have since been operated with an NO<sub>x</sub> removal efficiency over 80% and 5 ppm of unreacted NH<sub>3</sub>. An ammonium bisulfate problem occurred in the air preheater during the initial stage of operation when unreacted NH<sub>3</sub> was about 10 ppm.

The small amount of ammonia contained in the flue gas after SCR is caught by the wet FGD system. The FGD scrubbing liquor also contains nitrates derived from NO<sub>x</sub>. In order to reduce the nitrogen concentration to below 10 ppm in the FGD system wastewater, a conventional activated sludge treatment system has been constructed by Hitachi Zosen.

The total investment cost for the demonstration plant was 8 million yen including the cost of the hot ESPs, air preheaters, fans and wastewater treatment system. This cost is relatively high, due to the expense of retrofitting, as well as the cost of equipment required for the demonstration tests. According to EPDC personnel, the investment cost for an SCR system designed to remove 80% of the NO<sub>x</sub> from coal-fired boiler flue gas was 7,000 yen/kW in 1981. Assuming a 2-year catalyst life, the annualized cost for this same system was about 0.6 yen/kWhr (including a 7-year depreciation schedule).

#### 4.9 SCR COSTS

##### 4.9.1 Investment Costs

Table 4-20 shows the investment costs of 9 SCR plants for utility boilers. Chubu Electric's 2 SCR plants for LNG-fired boilers at its Chita Station



TABLE 4-20. INVESTMENT COSTS OF SCR PLANTS FOR UTILITY BOILERS

| Company           | Station       | Fuel | Size<br>(MW) | N/R            | NO <sub>x</sub><br>removal (%) | Outlet<br>NO <sub>x</sub> (ppm) | Vendor           | Start-<br>Up | Cost<br>(yen/kw)   |
|-------------------|---------------|------|--------------|----------------|--------------------------------|---------------------------------|------------------|--------------|--------------------|
| Chubu Electric    | Chita         | LNG  | 700          | N <sup>a</sup> | 80                             | 8                               | BH <sup>c</sup>  | 1978         | 2400               |
|                   |               | LNG  | 700          | N <sup>b</sup> | 80                             | 8                               | BH               | 1978         | 2400               |
|                   |               | Oil  | 700          | R              | 80                             | 18                              | MHI <sup>d</sup> | 1980         | 3600               |
| Chugoku Electric  | Kudamatsu     | Oil  | 375          | R              | 80                             | 32                              | IHI <sup>e</sup> | 1979         | 5900               |
|                   |               | Oil  | 700          | N              | 80                             | 26                              | IHI              | 1979         | 3200               |
|                   |               | Coal | 175          | R              | 50                             | 200                             | MHI              | 1980         | 9700 <sup>g</sup>  |
| Hokkaido Electric | Tomato-Atsuma | Coal | 350x1/4      | N              | >80                            | >40                             | BH               | 1980         | 10000 <sup>h</sup> |
| EPDC              | Takehara      | Coal | 250x1/2      | R              | 80                             | 80                              | BH               | 1981         | 7000 <sup>h</sup>  |
|                   |               | Coal | 250x1/2      | R              | 80                             | 80                              | KHI <sup>f</sup> | 1981         | 7000 <sup>h</sup>  |

<sup>a</sup>New<sup>b</sup>Retrofit<sup>c</sup>Babcock Hitachi<sup>d</sup>Mitsubishi Heavy Industries<sup>e</sup>Ishikawajima-Harima Heavy Industries<sup>f</sup>Kawasaki Heavy Industries Reactor has a capacity for 80% NO<sub>x</sub> removal.<sup>g</sup>Including boiler modification for economizer by-pass.<sup>h</sup>Rough approximation

are less costly (2400 yen/kW) than the other plants because they use clean gas treatment which permits the use of small amounts of a pellet catalyst with an SV of 20,000 hr<sup>-1</sup>. The SCR plant for the existing oil-fired boiler at the Chita Station cost 3,600 yen/kW using a honeycomb catalyst with an SV of 5,100 hr<sup>-1</sup>.

Chugoku Electric's SCR plants for oil-fired boilers at the Kudamatsu Station cost 5,900 yen/kW for the existing boiler and 3,200 yen/kW for the new boilers. Both systems use a honeycomb catalyst with an SV of about 5,100 hr<sup>-1</sup>. The relatively high cost of the plant for the existing boiler was a result of the cost of the extensive ductwork required for retrofitting, and the installation of new fans needed to compensate for the pressure drop caused by the SCR system (Section 4.3). The SCR plant for the existing oil-fired boiler at the Chita Station did not require an additional fan because the existing boiler fan was able to compensate for the increased pressure drop on its own.

The SCR plant for the existing coal-fired boiler at the Shimonoseki Station cost nearly 10,000 yen/kW including the cost for the boiler modification needed for installation of the economizer by-pass system (Section 4.4). Hokkaido Electric's SCR plant at the Tomato-Atsuma Station cost about 10,000 yen/kW and has a capacity of treating one-fourth of the flue gas from a new 350 MW boiler. The relatively high cost of this SCR system for a new boiler may be due to the small size of the plant (88 MW equivalent) and the fact that it removes 90% of NO<sub>x</sub>. EPDC's two SCR plants for existing coal-fired boilers at the Takehara Station cost about 7,000 yen/kW each. Generally speaking, an SCR plant which achieves 80% NO<sub>x</sub> removal for a new coal-fired utility boiler may cost 6,000 - 8,500 yen, depending on inlet SO<sub>x</sub> and NO<sub>x</sub> concentrations and the amount of unreacted NH<sub>3</sub> allowed.

#### 4.9.2 Estimated Investment and Annualized Costs

Tables 4-21 and 4-22 show the estimated investment and annualized costs of SCR for new 700-MW utility boilers burning coal, oil, and gas. In preparing these cost estimates the following assumptions were made, based on a study of the costs of commercial and demonstration SCR plants.

TABLE 4-21. CALCULATED COSTS FOR AN SCR PLANT FOR A NEW 700 MW COAL-FIRED BOILER (70% Boiler Utilization 4,292,000 Btu/hr/year, 1981 yen)  
(Flue Gas flow rate: 2,300,000 Nm<sup>3</sup>/hr; honeycomb catalyst: ceramic square type; 3.5 million yen/m<sup>2</sup>, 2 year life)

| Boiler basis                                                       | Parameter                                                | High S Coal            |                        | Low S Coal             |                        |
|--------------------------------------------------------------------|----------------------------------------------------------|------------------------|------------------------|------------------------|------------------------|
| Design data                                                        | NO <sub>x</sub> , ppm                                    | 600                    | 300                    | 300                    | 300                    |
|                                                                    | SO <sub>2</sub> , ppm                                    | 2500                   | 2500                   | 600                    | 600                    |
|                                                                    | Particulates, Nm <sup>3</sup>                            | 15-25 <sup>a</sup>     | 15-25 <sup>a</sup>     | 15-25 <sup>a</sup>     | 0.05-0.20 <sup>j</sup> |
|                                                                    | Catalyst size, mm                                        | 7.4 + 1.6 <sup>b</sup> | 7.4 + 1.6 <sup>b</sup> | 7.4 + 1.6 <sup>b</sup> | 6.6 + 1.4 <sup>b</sup> |
|                                                                    | NH <sub>3</sub> emissions, ppm                           | 4-5                    | 4-5                    | 4-5                    | 2-3                    |
| Investment costs                                                   | NO removal, %                                            | 80                     | 80                     | 80                     | 80                     |
|                                                                    | NH <sub>3</sub> /NO <sub>x</sub> mole ratio <sup>a</sup> | 0.82                   | 0.83                   | 0.83                   | 0.82                   |
|                                                                    | Space velocity, hr <sup>-1</sup>                         | 2200                   | 2700                   | 2200                   | 3000                   |
|                                                                    | Catalyst volume, m <sup>3</sup>                          | 1045                   | 852                    | 767                    | 767                    |
|                                                                    | Reactor pressure drop, mm/H <sub>2</sub> O               | 130                    | 115                    | 110                    | 110                    |
| Annual costs                                                       | Power consumption, %                                     | 0.20                   | 0.18                   | 0.22                   | 0.19                   |
|                                                                    | Catalyst, 10 <sup>3</sup> yen                            | 3.66                   | 2.98                   | 2.68                   | 2.68                   |
|                                                                    | Other, 10 <sup>3</sup> yen <sup>b</sup>                  | 2.25                   | 2.10                   | 2.00                   | 2.00                   |
|                                                                    | Total, 10 <sup>3</sup> yen <sup>b</sup>                  | 5.91                   | 5.08                   | 4.68                   | 4.68                   |
|                                                                    | Total, yen/kWh <sup>c</sup>                              | 8440                   | 7260                   | 6690                   | 6690                   |
| Annualized cost, yen/kWh                                           | Fixed cost, 10 <sup>3</sup> yen <sup>c</sup>             | 0.92                   | 0.83                   | 0.77                   | 0.77                   |
|                                                                    | Catalyst, 10 <sup>3</sup> yen <sup>c</sup>               | 1.83                   | 1.49                   | 1.34                   | 1.34                   |
|                                                                    | Ammonia, 10 <sup>3</sup> yen <sup>c</sup>                | 0.53                   | 0.27                   | 0.27                   | 0.26                   |
|                                                                    | Other, 10 <sup>3</sup> yen <sup>c</sup>                  | 0.20                   | 0.18                   | 0.16                   | 0.16                   |
|                                                                    | Total, 10 <sup>3</sup> yen <sup>c</sup>                  | 3.48                   | 2.77                   | 2.54                   | 2.53                   |
| Cost effectiveness, yen/Nm <sup>3</sup> of NO <sub>x</sub> removed | dollars/lb of NO <sub>x</sub> removed <sup>d</sup>       | 0.81                   | 0.65                   | 0.59                   | 0.59                   |
|                                                                    |                                                          | 514                    | 826                    | 749                    | 749                    |
|                                                                    |                                                          | 0.45                   | 0.73                   | 0.66                   | 0.66                   |

<sup>a</sup>Percent of power generated by the boiler  
<sup>b</sup>Including civil engineering and test operation  
<sup>c</sup>10% of catalyst and 25% of investment excluding catalyst  
<sup>d</sup>Catalyst cost divided by life (years)

<sup>e</sup>At 100,000 yen/ton

<sup>f</sup>Mainly for power (18 yen/kWh)

<sup>g</sup>41 = 2250, NO<sub>x</sub> as NO<sub>2</sub>

<sup>h</sup>Channel diameter plus wall thickness

<sup>i</sup>With full dust load

<sup>j</sup>Leaving a hot ESP

TABLE 4-22. CALCULATED COSTS FOR SCR FOR NEW 700 MW OIL- AND GAS-FIRED BOILERS (70% boiler utilization 4,292,000 kWhr/year) (1981 costs; flue gas flow rate: 2,000,000 Nm<sup>3</sup>/hr; ceramic square honeycomb and pellet catalysts)

| Boiler basis       | Parameter                                                     | High S Oil             | Low S Oil              | Low S Oil              | Gas                     |
|--------------------|---------------------------------------------------------------|------------------------|------------------------|------------------------|-------------------------|
| Design data        | Fuel                                                          |                        |                        |                        |                         |
|                    | NO <sub>x</sub> , ppm                                         | 200                    | 200                    | 100                    | 60                      |
|                    | SO <sub>x</sub> , ppm                                         | 1,500                  | 100                    | 100                    | 1                       |
|                    | Particulates, g/Nm <sup>3</sup>                               | 0.05-0.20              | 0.02-0.05              | 0.02-0.05 <sup>d</sup> | 0.005-0.03 <sup>d</sup> |
|                    | Catalyst type                                                 | Honeycomb              | Honeycomb              | Honeycomb              | Pellet                  |
|                    | Catalyst size, mm                                             | 6.6 + 1.4 <sup>h</sup> | 5.8 + 1.2 <sup>h</sup> | 5.8 + 1.2 <sup>h</sup> | 5                       |
|                    | Catalyst life, year                                           | 3                      | 3                      | 3                      | 4                       |
|                    | Catalyst cost, 10 <sup>3</sup> yen/m <sup>3</sup>             | 3.3                    | 3.3                    | 3.3                    | 3.0                     |
|                    | NO <sub>x</sub> emissions, ppm                                | 2-3                    | 4-5                    | 4-5                    | 6-8                     |
|                    | NO removal, %                                                 | 80                     | 80                     | 80                     | 80                      |
| Investment cost    | HHV/NO mole ratio                                             | 0.83                   | 0.93                   | 0.84                   | 0.98                    |
|                    | Space velocity, hr <sup>-1</sup>                              | 2800                   | 2000                   | 3100                   | 3700                    |
|                    | Catalyst volume, m <sup>3</sup>                               | 714                    | 1000                   | 463                    | 392                     |
|                    | Reactor pressure drop, mm/H <sub>2</sub> O                    | 120                    | 140                    | 105                    | 115                     |
|                    | Power consumption, %                                          | 0.17                   | 0.20                   | 0.16                   | 0.17                    |
|                    | Catalyst, 10 <sup>3</sup> yen                                 | 2.36                   | 3.30                   | 1.53                   | 2.13                    |
|                    | Other, 10 <sup>3</sup> yen <sup>b</sup>                       | 2.00                   | 2.25                   | 1.70                   | 1.90                    |
|                    | Total, 10 <sup>3</sup> yen <sup>b</sup>                       | 4.36                   | 5.55                   | 3.23                   | 4.03                    |
|                    | Total, yen/kW <sup>c</sup>                                    | 6230                   | 7930                   | 4610                   | 5760                    |
|                    | Fixed cost, 10 <sup>3</sup> yen <sup>c</sup>                  | 0.73                   | 0.89                   | 0.58                   | 0.69                    |
| Annual costs       | Catalyst, 10 <sup>3</sup> yen <sup>d</sup>                    | 0.79                   | 1.10                   | 0.31                   | 0.71                    |
|                    | Ammonia, 10 <sup>3</sup> yen <sup>e</sup>                     | 0.16                   | 0.17                   | 0.16                   | 0.18                    |
|                    | Other, 10 <sup>3</sup> yen <sup>f</sup>                       | 0.20                   | 0.24                   | 0.18                   | 0.19                    |
|                    | Total, 10 <sup>3</sup> yen                                    | 1.88                   | 2.40                   | 1.43                   | 1.77                    |
| Annualized cost    | (yen/kW/hr)                                                   | 0.44                   | 0.56                   | 0.33                   | 0.41                    |
|                    | (yen/Nm <sup>3</sup> of NO <sub>x</sub> removed) <sup>g</sup> | 958                    | 1087                   | 719                    | 794                     |
| Cost effectiveness | (dollars/lb of NO <sub>x</sub> removed) <sup>h</sup>          | 0.84                   | 0.96                   | 0.63                   | 0.70                    |
|                    |                                                               |                        |                        |                        |                         |

<sup>a</sup> Percent of power generated by the boiler including civil engineering and test operation  
<sup>b</sup> 10% of catalyst and 25% of investment excluding catalyst  
<sup>c</sup> Catalyst cost divided by life (years)  
<sup>d</sup> At 100,000 ysm/ton  
<sup>e</sup> Mainly for power (21 yen/kWh)  
<sup>f</sup> \$1 = ¥250, NH<sub>3</sub> as NO<sub>x</sub>  
<sup>g</sup> Channel diameter plus wall thickness  
<sup>h</sup> With full dust load  
<sup>i</sup> Leaving a hot ESP

- (1) As shown in Figure 4-36, flue gas from the boiler economizer is treated in the two trains of the SCR system. In most systems, the gas is first injected with ammonia and sent into the SCR reactor. The exception is the low-dust system for coal (C in Figure 4-36) in which the flue gas is sent through a hot ESP and then into a reactor.
- (2) A square honeycomb catalyst is used except in the case of the the system for the gas-fired boiler which uses a pellet catalyst. The channel diameter of the honeycomb is 7.4 mm for coal with a full dust load, 6.6 mm for coal with the low-dust system and high-sulfur oil, and 5.8 mm for low-sulfur oil. The catalyst cost is 3.5 million yen/m<sup>3</sup> for coal, 3.3 million yen for oil, and 3 million yen for gas. (Plate catalysts may be used instead of honeycombs for the same or a slightly lower cost.)
- (3) Unreacted NH<sub>3</sub> is maintained at 4-5 ppm for coal with a full dust load and low-sulfur oil. It is maintained at 2-3 ppm for coal with a low-dust system and high-sulfur oil because, in these cases, ammonium bisulfate deposition in the air preheater may become a serious problem if the unreacted NH<sub>3</sub> concentration is any higher.
- (4) NO<sub>x</sub> removals of 80% and 90% were assumed, which actually require 81-82% and 91-92% removal, respectively. For 90% NO<sub>x</sub> removal, 35-40% more catalyst is used than for 80% removal. A higher inlet NO<sub>x</sub> concentration also requires a larger amount of catalyst.
- (5) The catalyst-induced SO<sub>2</sub> oxidation ratio is maintained below 0.5% for high-sulfur fuels and below 1% for low-sulfur fuels.
- (6) The annual power generation is 4,292,499 MW (70% of full capacity).

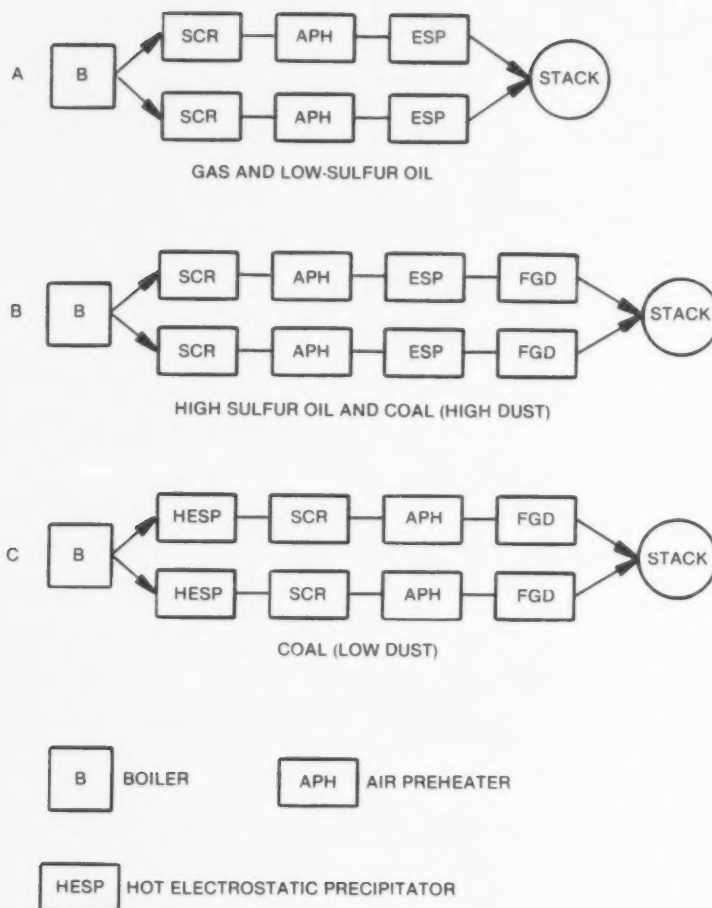


Figure 4-36 Flue Gas Treatment Systems.

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- (7) The investment cost includes costs for reactor, catalyst, ducts, ammonia tank and injection system, soot blowing system, control system, civil engineering services, and test operation.
- (8) The fixed capital cost includes a 25% investment cost excluding catalyst expense and 10% interest for the initial charge of the catalyst.
- (9) The catalyst life is 2 years for coal, 3 years for oil, and 4 years for gas. The annualized cost includes the catalyst cost divided by the catalyst life (years).
- (10) The cost of ammonia is 100,000 yen (\$400)/ton. The power cost is 18 yen/kWhr for coal and 21 yen/kWhr for oil and gas.

Table 4-21 shows that the investment cost for 80% NO<sub>x</sub> removal is 8,440 and 7,260 yen/kW for high-sulfur coal with 600 and 300 ppm inlet NO<sub>x</sub> concentrations, respectively. The cost for low-sulfur coal is 6,690 yen/kW for both the high-dust and low-dust systems. Compared with the high-dust system, the low-dust system uses the same amount of more efficient catalyst to maintain a lower level of unreacted NH<sub>3</sub>. The investment cost for 90% NO<sub>x</sub> removal is about 30% higher than that for 80% removal. The catalyst cost makes up over 55% of the investment cost for 80% removal and over 65% for 90% removal.

The annualized cost for 80% NO<sub>x</sub> removal is 0.81 and 0.65 yen/kWhr for high sulfur coal with 600 and 300 ppm inlet NO<sub>x</sub> concentrations, respectively, and is 0.59 yen/kWhr for low-sulfur coal. Ninety percent NO<sub>x</sub> removal costs about 30% more than 80% removal.

Although the annualized cost for NO<sub>x</sub> removal with 600 ppm inlet NO<sub>x</sub> is about 25% more than that for 300 ppm NO<sub>x</sub>, the cost effectiveness is much lower --- 45 cents vs. 73 cents per lb of NO<sub>x</sub> removed for 80% removal. With 90% NO<sub>x</sub> removal it is nearly 20% more cost effective to remove NO<sub>x</sub> from gas containing 300 ppm than from gas with 600 ppm NO<sub>x</sub>.

In actual practice it is difficult to consistently maintain 90% NO<sub>x</sub> removal with less than 5 ppm of unreacted NH<sub>3</sub> when treating a large amount of NO<sub>x</sub>-rich flue gas such as that from a large coal-fired boiler. This is true for two reasons. First, the NO<sub>x</sub> concentration as well as the gas velocity may be considerably different in different areas of the large duct and reactor inlet. Second, the boiler load is not constant, resulting in a fluctuation in both gas volume and NO<sub>x</sub> concentration, and the NO<sub>x</sub> analyzer has a delay time of several minutes. In order to reduce NO<sub>x</sub> from a large boiler by 90%, the combination of combustion modification for 35-50% removal and SCR for 80-85% removal may be more practical and economical than the use of SCR by itself.

Table 4-22 lists the costs of SCR systems for oil- and gas-fired boilers. The most common type of SCR plant in Japan is used for 80% NO<sub>x</sub> reduction in flue gas from an oil-fired boiler containing about 100 ppm NO<sub>x</sub>. The investment cost is 3,860 yen/kW, the annualized cost 0.27 yen/kW. NO<sub>x</sub> removal of 200 ppm inlet NO<sub>x</sub> in low-sulfur oil flue gas costs about 20% more than this; removal of NO<sub>x</sub> from gas-fired boiler flue gas containing 60 ppm NO<sub>x</sub> costs about half as much.

SCR for boilers which burn high-sulfur oil may require about 60% more catalyst than those which burn low-sulfur oil, given the same inlet NO<sub>x</sub> concentration and NO<sub>x</sub> removal ratios. This occurs for two reasons: (1) In the high-sulfur oil system the catalyst is less reactive. This is because of the low SO<sub>2</sub> oxidation ratio and the larger channel diameter needed for the larger amount of dust. (2) It is necessary to maintain unreacted NH<sub>3</sub> at a lower level in the high-sulfur oil system in order to reduce ammonium bisulfate deposition in the air preheater. Thus, the SCR system costs for high-sulfur oil-fired boilers are about 40% more than those for low-sulfur oil-fired boilers and are similar to SCR system costs for low-sulfur coal-fired boilers.

The investment cost for an SCR system applied to an existing boiler may be 10-40% more than that for a new boiler because of the retrofitting requirements and the possible need for new fans. When an SCR system is applied to 150°C flue gas leaving an air preheater, the system investment cost may be 40-

60% more and the annualized cost 50-80% more than that for SCR applied at the economizer outlet because of the requirement for gas heating. Although low-temperature catalysts which work at 150-200°C have been developed, these catalysts experience ammonium bisulfate problems. Applying SCR to the economizer outlet is more economical than using low-temperature catalysts at the air preheater outlet, even for existing boilers.

#### 4.9.3 Power Generation and Flue Gas Treatment Costs

Table 4-23 gives estimated costs for a new coal-fired power station with flue gas treatment systems in Japan. The total investment cost is 220,00 yen/kW, 10% of which is for FGD, 32% for SCR, and 1.8 for ESP. The total annualized cost, including the cost of flue gas treatment is 18 yen/kW. Of the total amount, 10% is for FGD, 4% for SCR, and 0.5% for ESP. The annualized cost for this coal-fired station is less than the cost of an oil-fired power station that uses ESP without FGD and SCR.

TABLE 4-23. POWER GENERATION COST FOR A COAL-FIRED BOILER IN JAPAN (1981)

|                                                                                                                                    |         |
|------------------------------------------------------------------------------------------------------------------------------------|---------|
| Investment cost (yen/kW)                                                                                                           |         |
| ESP (99% removal)                                                                                                                  | 4,000   |
| SCR (80% NO <sub>x</sub> removal)                                                                                                  | 7,000   |
| FGD (90% SO <sub>2</sub> removal)                                                                                                  | 30,000  |
| Total Power Plant (including boiler, turbine, generator, coal treatment, flue gas treatment, plant site, and auxiliary facilities) | 260,000 |
| Annualized cost including capital cost (yen/kW <sub>hr</sub> )                                                                     |         |
| ESP                                                                                                                                | 0.1     |
| SCR                                                                                                                                | 0.7     |
| FGD                                                                                                                                | 1.9     |
| Total power cost (including flue gas treatment)                                                                                    | 18.0    |

#### 4.10 USE OF JAPANESE SCR TECHNOLOGY IN THE UNITED STATES

##### 4.10.1 Introduction

As Japanese SCR technology has become more reliable and less costly some U.S. utility companies have become interested in using it. Various Japanese SCR processes have been licensed to U.S. firms (Table 4-24) and a number of pilot and demonstration plants have been constructed.

The U.S. Environmental Protection Agency (EPA) sponsored an 0.5 MW pilot plant test of the Hitachi Zosen SCR process at Georgia Power Company's Mitchell Station. The Electric Power Research Institute (EPRI) constructed a 2.5 MW pilot plant which uses KHI's SCR system at Public Service Co. of Colorado's Arapahoe Station. Southern California Edison has constructed a 107.5 MW KHI SCR demonstration facility with a capacity of treating one-half of the gas from a 215 MW oil-fired boiler at its Huntington Beach Station. In addition, IHI's SCR catalyst will be used at an SCR pilot plant for an industrial boiler.

This section describes the pilot plant tests of the Hitachi Zosen process at Georgia Power Company's Mitchell Station.

##### 4.10.2 Hitachi Zosen Technology Pilot Plant Tests at the Mitchell Station (1)

Hitachi Zosen received an order from EPA for a 1,700 NM<sup>3</sup>/hr (0.5 MW equivalent) capacity demonstration SCR plant which would remove 90% of NO<sub>x</sub> from coal-fired boiler flue gas.

Chemico Air Pollution Control Corporation, Hitachi Zosen's North American licensee, constructed the demonstration plant at Georgia Power Company's Mitchell Station. The boiler burns Kentucky coal containing about 1% sulfur. For the test, flue gas (1,700 Nm<sup>3</sup>/hr) from the boiler economizer with a full dust load was used. Since the gas cools while passing through a long duct

TABLE 4-24. PRINCIPAL VENDOR CONTACTS FOR JAPANESE NO<sub>x</sub> SCR TECHNOLOGY (3)

| Process                                                         | Japan Representative                                                                                                                                                                             | U.S. Licensee or Partner                                                                                                                                                                    |
|-----------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Babcock-Hitachi<br>(Hitachi, Ltd.)                              | Hiroshi Kuroda<br>Kure Works. Babcock-<br>Hitachi K.K.<br>No. 6-9 Takara-Machi<br>Kure-shi, Hiroshima-Ken,<br>737, Japan<br>(0823) (21) 1161<br>Telex 6624-21 BNK KRE-J                          | Greg T. Bielawski<br>Babcock and Wilcox<br>FPG-ESC<br>P.O. Box 351<br>Barbarton, Ohio 44203<br>216/753-451                                                                                  |
| Hitachi-Zosen<br>(Hitachi Ship-<br>building and<br>Engineering) | Shingo Tanaka<br>Hitachi Shipbuilding &<br>Engineering Co., Ltd.<br>Palaceside Building<br>1-1, Hitotsubashi, 1-Chome<br>Chiyoda-Ku, Tokyo, Japan<br>Tokyo (213) 6611<br>Telex J22363 • J24490   |                                                                                                                                                                                             |
| Ishikawajima-<br>Harima<br>Heavy<br>Industries<br>(IHI)         | Nobuo Aoki<br>Ishikawajima-Harima Heavy<br>Industries Co., Ltd.<br>Tokyo Genboku Kaikan<br>30-13 • 5-chrome, Tokyo<br>Koto-Ku, Tokyo, 135, Japan<br>(03) 649-1111<br>Telex (IEI CO) J22232       | John Cvicker<br>Foster Wheeler Energy Corp<br>9 Peach Tree Hill Road<br>Livingston, NJ 07039<br>201/533-2687                                                                                |
| Kawasaki<br>Heavy<br>Industries<br>(KHI)                        | Senji Niwa<br>Kawasaki Heavy Industries,<br>Ltd.<br>14, 2-Chome<br>Higashikawasaki-Cho<br>Ikuta-Ku, Kobe, 650-91<br>Japan<br>Tel. Kobe (078) 671-5001<br>Telex 5624-032 KHI CPL J                | Joy Manufacturing<br>Western Precipitation Div.<br>P.O. Box 2744<br>Los Angeles, CA 90051<br>213/240-2300                                                                                   |
| Mitsubishi<br>Heavy<br>Industries<br>(MHI)                      | Tadamasa Sengoku<br>Mitsubishi Heavy Industries,<br>Ltd.<br>Shin-Tamachi Bldg.<br>34-6, Shiba 3-chome<br>Minato-Ku, Tokyo 108<br>Japan<br>(03) 455-5711<br>Telex J22282 HISHIJU<br>J28578 MHITAM | Donald J. Frey<br>Manager, Fuel Systems<br>Engineering<br>CE Power Systems<br>Combustion Engineering,<br>Inc.,<br>1000 Prospect Hill Road<br>Windsor, Conn. 16095<br>203/688-1911 Ext. 2241 |

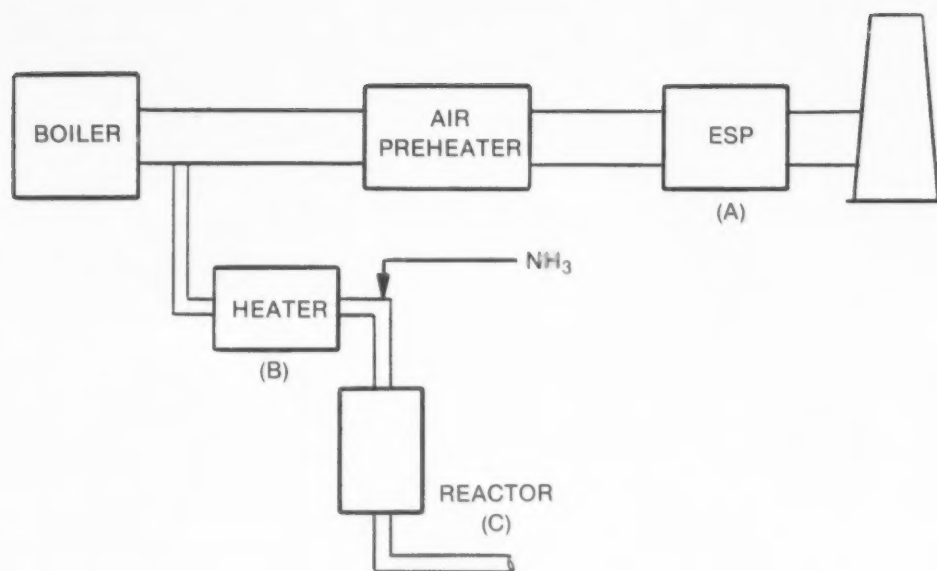


**Figure 4-37** SCR Pilot Plant and Fly Ash Sampling Points,  
Mitchell Station, Georgia Power Co.

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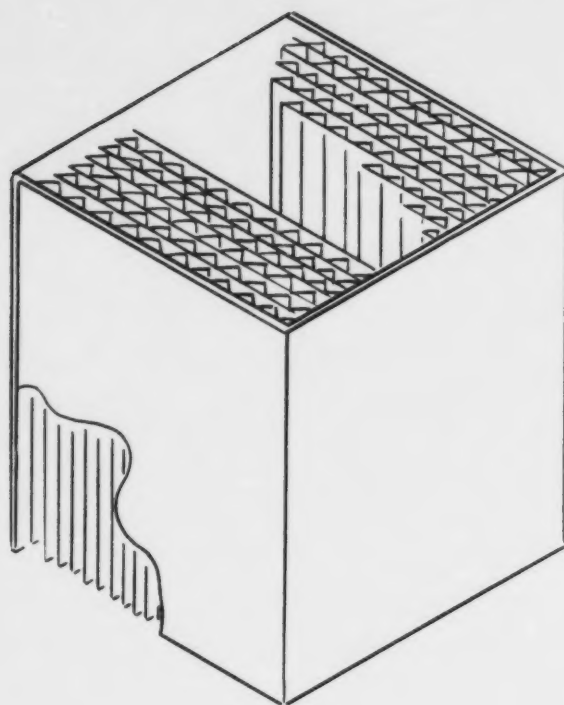


**Figure 4-38**    **NOXNON 600 Catalyst.**

(14" diameter), it is electrically heated to about 400°C and then injected with ammonia before it passes down through the SCR reactor (Figure 4-37).

A NOXNON 500 catalyst was used for the first and second pilot plant tests. The catalyst was prepared by treating the surface of a special alloy plate; it is similar in shape to the NOXNON 600 catalyst used for the third test (Figure 4-38).

The first test using the NOXNON 500 catalyst and an  $\text{NH}_3/\text{NO}_x$  mole ratio of 1.0 initially produced a 90%  $\text{NO}_x$  removal rate. However, this efficiency decreased during the course of the 2,000-hour test run as the pressure drop increased. Tests on the used catalyst showed that the decrease in efficiency was not caused by poisoning of the catalyst but instead, by fly ash deposition on the catalyst surface.

For the second test, a new NOXNON 500 catalyst was used and soot blowing was added. Despite these measures, the  $\text{NO}_x$  removal efficiency still decreased during the 2,000 hour test period.

A NOXNON 600 catalyst was used for the third test. The NOXNON 600 has a stainless steel mesh base which is coated with catalyst material and shaped as shown in Figure 4-38. The pitch of the NOXNON 600 catalyst is 14 mm whereas the NOXNON 500 has a pitch of 8 mm. Because of the wider pitch of the former catalyst, the reactor was lengthened for the third test to enable it to attain 90% removal. Use of this catalyst greatly reduced the reactor's dust clogging tendency.

Results of demonstration tests conducted from May through October 1980 using the NOXNON 600 catalyst are shown in Figure 4-39 (9). The results represent over 3500 hours of operation. During the first 90 days of operation the  $\text{NO}_x$  removal efficiency averaged over 90 percent. For the entire test period of 160 days of continuous operation, the average  $\text{NO}_x$  reduction was only slightly lower—89.8 percent. Figure 4-39 also illustrates that when it remains in the range of 2100 to 2400  $\text{Nm}^3/\text{hr}$ , the flow rate has essentially no effect on the SCR system's  $\text{NO}_x$  removal efficiency.

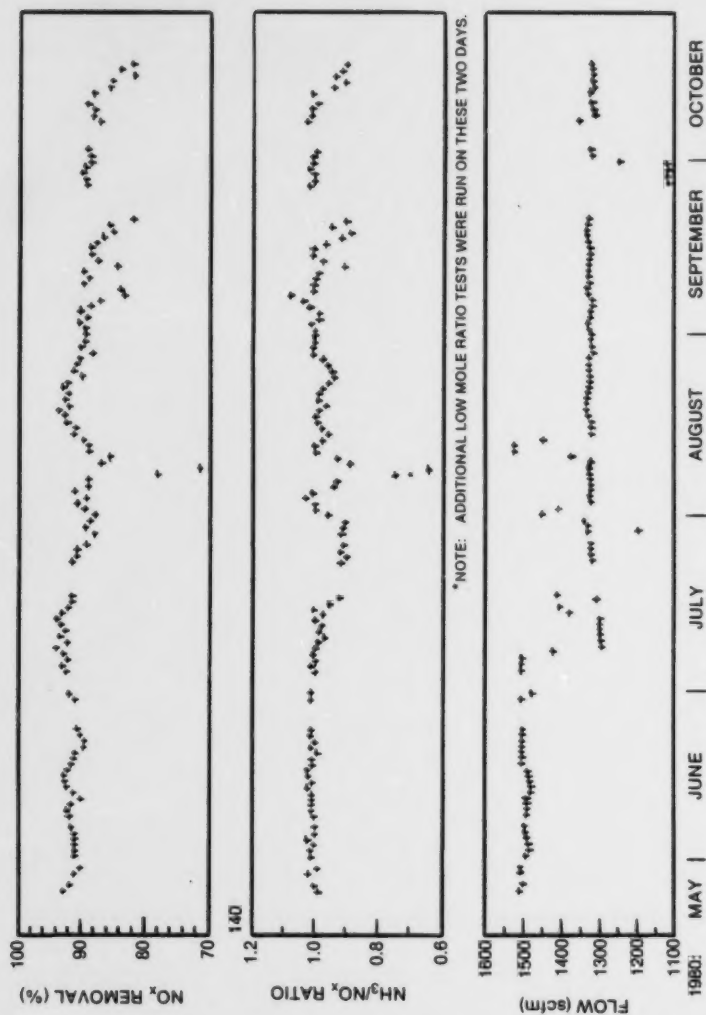


Figure 4-39 Demonstration Test Results from the SCR Pilot Plant, Mitchell Station, Georgia Power Co. (9)

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Since catalytic activity decreased slightly during the 3,500-hour test period, a regeneration technique was developed to restore the activity to its initial level.

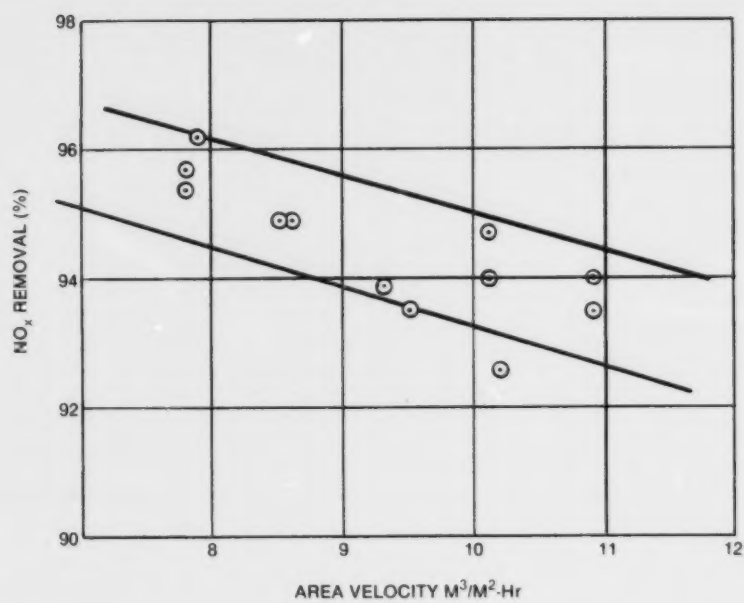
Figures 4-40 and 4-41 show the results of tests using NOXNON 600 with different area velocities and  $\text{NH}_3/\text{NO}_x$  mole ratios. Over 90%  $\text{NO}_x$  removal was attained with a mole ratio of 1.0 and an area velocity smaller than  $12 \text{ m}^3/\text{m}^2 \text{ hr}$ . However, with the mole ratio of 1.0, unreacted  $\text{NH}_3$  exceeds 30 ppm. One gas analysis at the pilot plant indicated that at 90%  $\text{NO}_x$  removal, unreacted  $\text{NH}_3$  reached about 50 ppm and that the  $\text{SO}_3$  content of the gas was 8.4 ppm at the reactor inlet and increased to 20.7 ppm at the outlet. (10)

#### 4.10.3 Evaluation

The SCR pilot plant tests at the Mitchell Station indicated that with a 90%  $\text{NO}_x$  removal, both unreacted  $\text{NH}_3$  and  $\text{SO}_3$  levels are high and can contaminate the fly ash. To lower unreacted  $\text{NH}_3$  to below 5 ppm, a mole ratio of 0.82-0.83 should be used to remove 82-83% of  $\text{NO}_x$ . In order to reduce  $\text{SO}_3$ , a low-oxidation, and therefore less active, catalyst should be used. An 80%  $\text{NO}_x$  removal efficiency appears to be a practical target for treating a large amount of flue gas with a high  $\text{NO}_x$  concentration.

The NOXNON 500 catalyst proved to have a considerable dust clogging problem. With its wider pitch, the NOXNON 600 performed well, but still was not free of the dust clogging problem. On the other hand, during Hitachi Zosen's SCR test at EPDC's Isogo Station, the NOXNON 500 catalyst experienced no dust clogging problem. This indicates a difference in the nature of the fly ash at the two test sites.

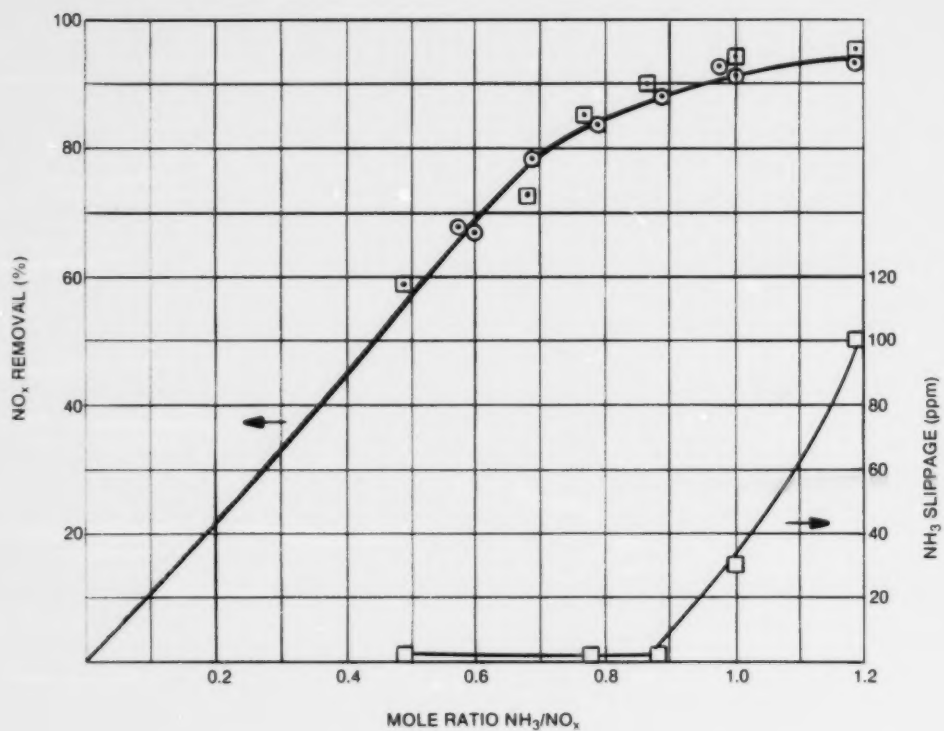
In order to determine the reason for this difference, the author tested samples of fly ash obtained from three locations at the Mitchell Station pilot plant (Figure 4-37, A, B, and C): the commercial ESP, the heater, and the reactor.



MOLE RATIO: 1.0  
REACTOR TEMP: 720°F  
INLET NO<sub>x</sub> CONCENTRATION: 400-450 ppm

Figure 4-40 NO<sub>x</sub> Removal vs. Area Velocity. (1)

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CATALYST: NOXNON 600  
 TEMP: 700-710°F  
 FLOW RATE: 1500 scfm  
 1300 scfm  
 INLET  $\text{NO}_x$ : 400-500 ppm

Figure 4-41  $\text{NO}_x$  Removal vs. Mole Ratio. (1)

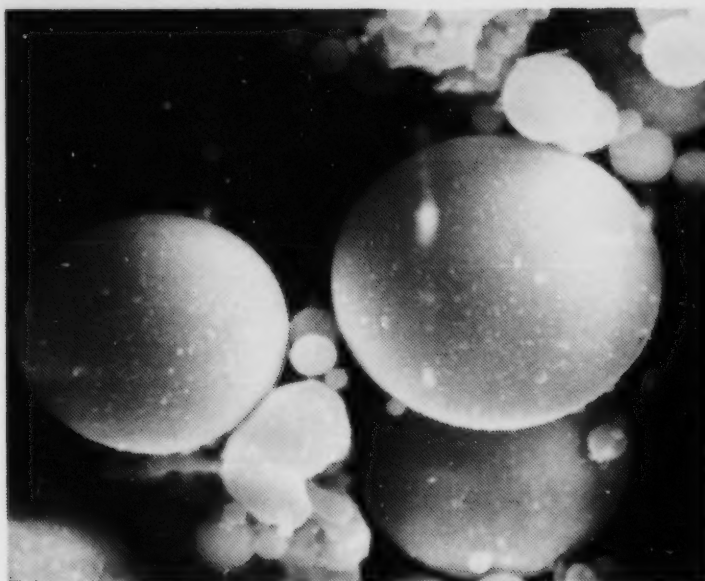
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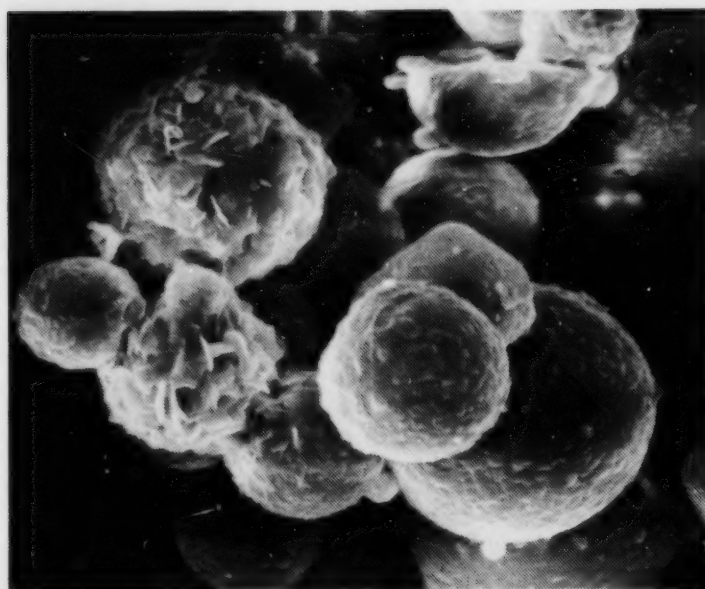
Figures 4-42 and 4-43 are scanning electron microscope photographs of the samples. The author compared these samples with fly ash samples obtained at SCR plants in Japan. The chemical composition of the samples is shown in Table 4-26. Ash A has a clean smooth surface similar to the Japanese ashes as shown in Figure 4-42. By contrast, ashes B and C have many deposits on their surface. Such deposits appear to give the ash an adhesive quality. Some of the ash B particles contain crystals which have grown perpendicularly on their surfaces as shown in Figure 4-42. This indicates crystal growth caused by gas phase reaction.

The author presumes that these deposits on the ash, including the well-grown crystals, were formed by the reaction of  $\text{SO}_2$  and metallic vapor in the combustion gas. It seems likely that a considerable amount of  $\text{SO}_2$  is formed in the heater at the Mitchell Station. This heater contains fine stainless steel tubes which are at a temperature above  $400^\circ\text{C}$ . Stainless steel has been known to act as a good oxidation catalyst of  $\text{SO}_2$  to  $\text{SO}_3$ . Although a similar heater has been used by Hitachi Zosen at Isogo, the  $\text{SO}_2$  content of the flue gases at the two stations are different---about 1,000 ppm at the Mitchell Station and about 300 ppm at Isogo. At the Mitchell Station a much larger amount of  $\text{SO}_3$  may form on the surface of the hot tubes. It is on these same tubes that the fly ash deposits and undergoes the reaction described above. It has been found that various metallic components in coal vaporize upon combustion and condense on the ash surface during cooling. As shown in Table 4-25, ashes B and C contain more than 10 times the amount of potassium that the Japanese ashes contain; potassium is volatile at high temperatures. Other metallic components also may be involved in the formation of the deposits.

The author presumes that the combination of those two factors caused deposit formation and made the ash adhesive; the deposits have a much lower melting point than that of the ash particles themselves and may be quite adhesive at  $400^\circ\text{C}$ . The well-grown crystals may have been formed while the ash remained on the surface of the stainless steel tube. Some of the ash particles may occasionally dislodge and deposit on the catalyst.

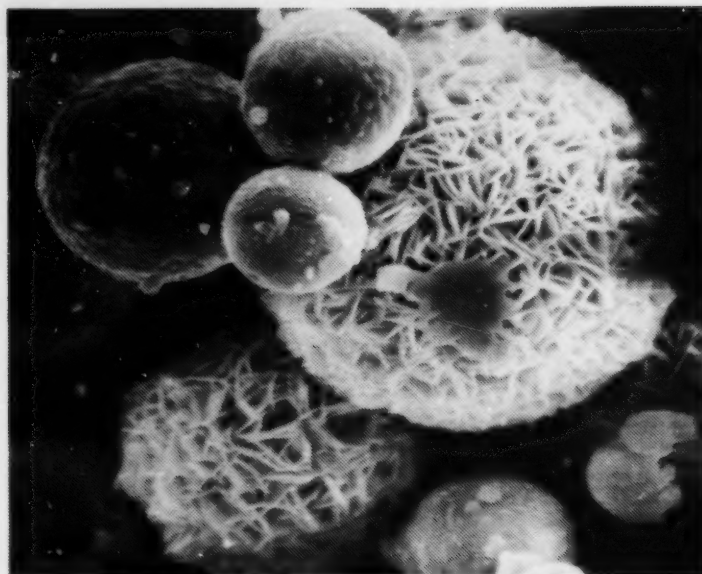


(A) (FROM ESP)



(B) (FROM HEATER)

**Figure 4-42** Scanning Electron Microscope Photographs of Fly Ash at Plant Mitchell (I) (x3000)



(B) (FROM HEATER)



(C) (FROM REACTOR)

**Figure 4-43** Scanning Electron Microscope Photographs of Fly Ash at Plant Mitchell (II) (x3000)

TABLE 4-25. COMPOSITION OF FLY ASH (%)

|                                | Mitchell Station |                | Isogo          |                |
|--------------------------------|------------------|----------------|----------------|----------------|
|                                | B                | C              | (1)            | (2)            |
| SiO <sub>2</sub>               | 48.0             | 47.8           | 45.1           | 44.5           |
| Al <sub>2</sub> O <sub>3</sub> | 32.1             | 31.3           | 21.5           | 22.2           |
| Fe <sub>2</sub> O <sub>3</sub> | 12.1             | 10.7           | 5.2            | 5.7            |
| TiO <sub>2</sub>               | 1.3              | 1.2            | 1.4            | 1.3            |
| CaO                            | 1.8              | 1.8            | 1.1            | 4.7            |
| MgO                            | 1.3              | 1.4            | 1.8            | 1.9            |
| Na <sub>2</sub> O              | 0.3              | 0.3            | 0.9            | 0.6            |
| K <sub>2</sub> O               | 2.8              | 3.0            | 0.08           | 0.24           |
| SO <sub>4</sub>                | — <sup>a</sup>   | — <sup>a</sup> | 9.1            | 5.3            |
| NH <sub>3</sub>                | — <sup>a</sup>   | 0.2            | — <sup>a</sup> | — <sup>a</sup> |

An example of dust clogging on an SCR catalyst in Japan took place during treatment of flue gas from an iron-ore sintering machine. The gas contained large amounts of SO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> dust, and potassium vapor which resulted in deposits of a double salt and potassium ferric sulfate on the catalyst.

Since ash A has a clean smooth surface and is not adhesive, it is possible that the fly ash at the Mitchell Station would not be adhesive if the stainless steel heater were not used. On the other hand, surfaces of ash particles obtained at Isogo, Takasago, and the Mitchell Station (A) are not entirely clean, but have many fine deposits, although the amount of deposition is far less than that of ashes B and C. Further study on the surface properties of these ashes may be needed.

A gas analysis of the SO<sub>2</sub> concentrations at the inlet and outlet of the SCR reactor at Mitchell indicates that the SO<sub>2</sub> oxidation ratio was about 1.2%. Although the oxidation ratio is not very high, a low-oxidation catalyst may be desirable for treating SO<sub>2</sub>-rich gas. In addition, oxidation at the catalyst surface may have promoted dust clogging.



Catalyst shape also has an effect on dust clogging. As shown in Figure 4-44, the wave catalyst has many corners with small angles in which the actual gas velocity is slow. This results in dust deposition in the corners and soot blowing does not efficiently remove these deposits. Triangle catalysts, such as NOXNON 500 and 600 also have a tendency for dust plugging at the corners. Hexagonal or simple plate catalysts are the best type of catalysts for avoiding dust plugging.

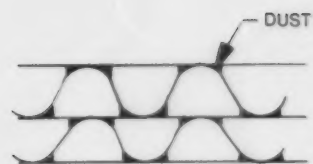
Dust plugging also may be prevented by using a suitably-shaped low oxidation catalyst along with an adequate gas velocity.

#### 4.10.4 Costs of SCR for Coal-Fired Boiler Applications in the U.S.

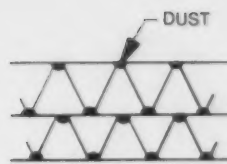
Tables 4-26 and 4-27 show the estimated investment and annual costs of SCR applied to a 500-MW coal-fired boiler in the U.S. for 90% removal using Hitachi Zosen's catalyst. The total investment cost equals \$51/kW and is close to the 10,760 yen for \$43/kW shown in Table 4-21 for 90% NO<sub>x</sub> removal with 600 ppm inlet NO<sub>x</sub>, although the basis of the cost calculation may be a little different. The total annual cost for a 7000-hour SCR operation period at the 500 MW plant is estimated at \$11,160,000. Assuming an average 90% load during operation hours, the annualized cost accounts for 3.54 mil/kWhr, which is slightly less than the cost shown in Table 4-21.

Tables 4-26, 4-27 and 4-21 show a variation in the estimated cost of the catalyst. Tables 4-26 and 4-27 assume the initial charge of the catalyst to be \$10.50/kW combined with a catalyst life of 1 year. Table 4-21 assumes the initial charge of the catalyst to be 5230 yen (\$20.90)/kW with a catalyst life of 2 years, yielding an annualized catalyst cost of \$10.50/kW.

In Japan, the life of an SCR catalyst used with a coal-fired boiler is usually guaranteed for one year although in practice it may last for 2 years. Only one catalyst has been used for 2 years (at Shimonoseki) and it operated at 50% removal. With regeneration, Hitachi Zosen's catalyst may be used for 2 years which would mean a lower annualized cost. On the other hand, a larger



(A) WAVE TYPE



(B) TRIANGLE TYPE



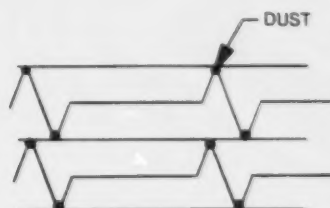
(C) SQUARE TYPE



(D) HEXAGONAL TYPE



(E) PARALLEL PLATE



(F) MODIFIED PLATE

Figure 4-44 Parallel Flow Catalysts and their Dust Clogging Tendencies.



TABLE 4-26. ESTIMATED CAPITAL INVESTMENT FOR A 500 MW APPLICATION OF THE HITACHI ZOSEN PROCESS IN THE U.S.<sup>a</sup> (9)

|                                                                          | Investment, \$   | % of total direct investment |
|--------------------------------------------------------------------------|------------------|------------------------------|
| <u>Direct Investment<sup>b</sup></u>                                     |                  |                              |
| NH <sub>3</sub> storage and injection                                    | 692,000          | 5.0                          |
| Reactor section                                                          | 10,247,000       | 74.7                         |
| Gas handling                                                             | 472,000          | 3.4                          |
| Air preheater modifications                                              | <u>1,534,000</u> | <u>11.2</u>                  |
| Sub-total direct investment (DI)                                         | 12,945,000       | 94.3                         |
| Services, utilities (0.06 x DI)                                          | <u>777,000</u>   | <u>5.7</u>                   |
| Total direct investment (TDI)                                            | 13,722,000       | 100.0                        |
| <u>Indirect Investment</u>                                               |                  |                              |
| Engineering design and supervision                                       | 298,000          | 2.2                          |
| Architect and engineering contractor                                     | 75,000           | 0.5                          |
| Construction expense<br>= 0.25 (TDI x 10 <sup>-6</sup> ) <sup>0.33</sup> | 2,198,000        | 16.0                         |
| Contractor fees = 0.096 (TDI x 10 <sup>-6</sup> ) <sup>0.76</sup>        | <u>703,000</u>   | <u>5.1</u>                   |
| Total indirect investment (IDI)                                          | 3,274,000        | 23.8                         |
| Contingency = 0.2 (TDI + IDI)                                            | <u>3,399,000</u> | <u>24.8</u>                  |
| Total fixed investment (TFI)                                             | 20,395,000       | 148.6                        |
| <u>Other Capital Charges</u>                                             |                  |                              |
| Allowance for startup and modifications<br>= (0.1) (TFI)                 | 2,040,000        | 14.9                         |
| Interest during construction<br>= (0.12) (TFI)                           | <u>2,447,000</u> | <u>17.8</u>                  |
| Total depreciable investment                                             | 24,882,000       | 181.3                        |
| Land                                                                     | 5,000            | -                            |
| Working capital                                                          | 270,000          | 3.4                          |
| Royalty fee                                                              | <u>300,000</u>   | <u>2.2</u>                   |
| TOTAL CAPITAL INVESTMENT                                                 | 25,657,000       | 186.9                        |

<sup>a</sup>Basis: 500 MW new coal-fired power plant, 3.5% sulfur coal, 90% NO<sub>x</sub> removal. Midwest plant location. Represents project beginning mid-1977, ending mid-1980. Average basis for scaling, mid-1979. Investment requirements for fly ash disposal excluded. Construction labor shortages with overtime pay incentive not considered.

<sup>b</sup>Each item of direct investment includes total equipment costs plus installation labor, and material costs for electrical, piping, ductwork, foundations, structural, instrumentation, insulation, and site preparation.

TABLE 4-27. ESTIMATED AVERAGE ANNUAL REVENUE REQUIREMENTS FOR A 500 MW APPLICATION OF THE HITACHI ZOSSEN PROCESS IN THE U.S.<sup>a</sup> (9)

| Item                                                           | Annual Quantity  | Unit Cost (\$)   | Annual Cost (\$) | % of annual revenue required |
|----------------------------------------------------------------|------------------|------------------|------------------|------------------------------|
| <b>Direct Costs</b>                                            |                  |                  |                  |                              |
| Raw materials                                                  |                  |                  |                  |                              |
| NH <sub>3</sub>                                                | 5.28x10 kg       | 0.165/kg         | 871,000          | 7.8                          |
| Catalyst                                                       |                  |                  | 5,250,000        | 47.0                         |
| Total raw materials                                            |                  |                  | 6,121,000        | 54.8                         |
| Conversion costs                                               |                  |                  |                  |                              |
| Operating labor and supervision                                | 8,760 labor hrs. | 12.50/labor hrs. | 110,000          | 1.0                          |
| Utilities                                                      |                  |                  |                  |                              |
| Steam                                                          | 85,800 GJ        | 1.90/GJ          | 163,000          | 1.5                          |
| Electricity                                                    | 18,226,000 kWh   | 0.029/kWh        | 529,000          | 4.8                          |
| Heat credit                                                    | 125,200 GJ       | -1.90/GJ         | (214,000)        | (1.9)                        |
| Maintenance = 0.04 x TDI                                       |                  |                  | 549,000          | 4.9                          |
| Analyses                                                       | 2,920 labor hrs. | 17.00/labor hrs. | 50,000           | 0.4                          |
| Total conversion costs                                         |                  |                  | 1,187,000        | 10.7                         |
| Total direct costs                                             |                  |                  | 7,308,000        | 65.5                         |
| <b>Indirect Costs</b>                                          |                  |                  |                  |                              |
| Capital charges                                                |                  |                  |                  |                              |
| Depreciation = (0.06) (total depreciable investment)           |                  |                  | 1,493,000        | 13.3                         |
| Average cost of capital = (0.086) x (total capital investment) |                  |                  | 2,207,000        | 19.8                         |
| Overheads                                                      |                  |                  |                  |                              |
| Plant = (0.5) (conversion costs minus utilities)               |                  |                  | 355,000          | 3.2                          |
| Administrative = (0.1) (operating labor costs)                 |                  |                  | 11,000           | 0.1                          |
| Total indirect costs                                           |                  |                  | 4,066,000        | 36.4                         |
| Spent catalyst disposal                                        |                  |                  | (214,000)        | (1.9)                        |
| Gross average revenue requirement                              |                  |                  | 13,160,000       | 100.0                        |
| TOTAL ANNUAL REVENUE REQUIREMENTS                              |                  |                  | 13,160,000       | 100.0                        |

<sup>a</sup>Basis: 500 MW new coal-fired power plant, 3.5% S coal, 90% NO<sub>x</sub> reduction, 90% SO<sub>2</sub> removal. Midwest power plant location, 1980 revenue requirements. Remaining life of power plant = 30 years. Plant on line 7000 hr/yr. Plant heat rate equals 9.5 MG/kWh. Investment and revenue requirement for disposal of fly ash excluded. Total direct investment \$73,722,000; total depreciable investment \$24,882,000; and total capital investment \$24,657,000.

amount of catalyst than that upon which these figures are based may be needed to reduce unreacted  $\text{NH}_3$  to a level of 5 ppm or below.

In the U.S., the reduction of unreacted  $\text{NH}_3$  may be important for coal-fired boilers. This is because it is necessary to maintain an appropriate ammonia content in the large amounts of fly ash and sludge produced by the lime/limestone FGD process. Based on this assumption, catalyst costs in the U.S. may be similar to those listed in Table 4-21.

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## SECTION 5

### SCR FOR INDUSTRIAL GAS SOURCES

#### 5.1 GENERAL DESCRIPTION

##### 5.1.1 SCR Units for Industrial Gas Sources

SCR units for industrial gas sources with a capacity greater than 10,000 Nm<sup>3</sup>/hr are listed in Tables 5-1 through 5-3. Of a total of 62 units, 58 are commercial and four are test units (Nos. 33, 35, 65, and 72).

Most of the SCR units were constructed between 1975 and 1978, when the ambient NO<sub>x</sub> standard was extremely stringent—0.02 ppm as a daily average. This standard is equivalent to 0.01 ppm as a yearly average and is less than half of the 0.05 ppm equivalent U.S. daily average standard. In order to achieve this stringent standard, local governments reduced NO<sub>x</sub> as much as possible.

Few SCR units for industrial gas sources have been constructed since 1979 partly because the ambient standard was relaxed in 1978 to 0.04–0.06 ppm as a daily average, and partly because of the economic recession which slowed the construction of new factories requiring NO<sub>x</sub> flue gas treatment.

Most of the SCR units use granular (or pellet) catalysts for the following reasons: (1) many units treat clean flue gas; (2) parallel flow catalysts were not well developed before 1978; and (3) some of the units use granular catalysts in a moving bed. Moving bed systems can remove 70–80% of the dust



TABLE 5-1. SCR PLANTS FOR OIL, PETROCHEMICAL, AND GAS COMPANIES (Gas Flow Greater than 10,000 Nm<sup>3</sup>/hr)

| No.                            | User                   | Plant Site | Gas Source | Fuel               | Capacity<br>(1,000 Nm <sup>3</sup> /hr) | New or<br>Retrofit | Vendor              | Catalyst        | Start Up |
|--------------------------------|------------------------|------------|------------|--------------------|-----------------------------------------|--------------------|---------------------|-----------------|----------|
| <u>Oil Companies</u>           |                        |            |            |                    |                                         |                    |                     |                 |          |
| 1                              | Fuji Oil               | Sodegaura  | CO Boiler  | CO, H <sub>2</sub> | 70                                      | R                  | JGC                 | pp <sup>b</sup> | 1976     |
| 2                              | Fuji Oil               | Sodegaura  | Boiler     | HO                 | 200                                     | N                  | Mitsubishi H.I.     | H <sup>c</sup>  | 1978     |
| 3                              | Idemitsu Kosen         | Ancasaka   | Furnace    | FCC gas            | 350                                     | R                  | Hitachi Zosen       | G <sup>d</sup>  | 1975     |
| 4                              | Kansai Oil             | Sakai      | Boiler     | HO                 | 150                                     | R                  | Hitachi Zosen       | G               | 1979     |
| 5                              | Kashima Oil            | Kashima    | Furnace    | Offgas             | 58                                      | R                  | JGC                 | pp              | 1975     |
| <u>Petrochemical Companies</u> |                        |            |            |                    |                                         |                    |                     |                 |          |
| 6                              | Chiba Pet. Chem.       | Chiba      | Boiler     | HO                 | 10                                      | R                  | Ube Kosau           | G               | 1975     |
| 7                              | Idemitsu Pet. Chem.    | Ancasaka   | Furnace    | LHG                | 300                                     | R                  | Mitsui Toatsu       | G               | 1977     |
| 8                              | Mitsui Pet. Chem.      | Chiba      | Boiler     | FCC Gas            | 240                                     | R                  | Mitsui Engineering  | G               | 1975     |
| 9                              | Mitsubishi Pet. Chem.  | Yokoteichi | Boiler     | HO                 | 150                                     | R                  | Hitachi Ltd.        | G               | 1976     |
| 10                             | Nihon Pet. Chem.       | Chiba      | Boiler     | HO                 | 100                                     | R                  | Mitsubishi Kakoki   | T <sup>e</sup>  | 1976     |
| 11                             | Osaka Pet. Chem.       | Sakai      | Furnace    | Offgas             | 91                                      | R                  | Mitsui Toatsu       | G               | 1976     |
| 12                             | Shindaiyowa Pet. Chem. | Yokoteichi | Boiler     | HO                 | 440                                     | R                  | Hitachi Zosen       | G               | 1975     |
| 13                             | Ukishima Pet. Chem.    | Chiba      | Boiler     | HO                 | 260                                     | N                  | Mitsui Engineering  | T               | 1978     |
| <u>Gas Companies</u>           |                        |            |            |                    |                                         |                    |                     |                 |          |
| 14                             | Osaka Gas              | Senpoku    | Generator  | Naphtha            | 64                                      | R                  | Mitsubishi H.I.     | G               | 1975     |
| 15,16                          | Osaka Gas              | Senpoku    | Boiler     | Gas                | 30 x 2                                  | R                  | Mitsubishi H.I.     | G               | 1976     |
| 17,18                          | Toho Gas               | Chiba      | Generator  | Naphtha            | 42 x 2                                  | R                  | Mitsubishi Kakoki   | G               | 1977     |
| 19                             | Toho Gas               | Chiba      | Boiler     | Kerosene           | 30                                      | R                  | Mitsubishi Kakoki   | G               | 1977     |
| 20                             | Toho Gas               | Sorami     | Reformer   | Naphtha            | 19                                      | R                  | Mitsubishi Kakoki   | G               | 1976     |
| 21,22                          | Toho Gas               | Sorami     | Reformer   | Naphtha            | 31 x 2                                  | R                  | Sumitomo Chem. Eng. | G               | 1977     |
| 23                             | Toho Gas               | Sorami     | Boiler     | Naphtha            | 23                                      | R                  | Sumitomo Chem. Eng. | G               | 1977     |

<sup>a</sup> Heavy Oil<sup>b</sup> Parallel Passage Reactor<sup>c</sup> Honeycomb<sup>d</sup> Granular<sup>e</sup> Tubular



TABLE 5-2. SCR PLANTS FOR STEEL AND METAL INDUSTRIES (Larger than 10,000 Nm<sup>3</sup>/hr)

| No.            | User            | Plant Site | Gas Source        | Fuel              | Capacity<br>(1,000 Nm <sup>3</sup> /hr) | New or<br>Retrofit | Vendor            | Catalyst        | Start Up |
|----------------|-----------------|------------|-------------------|-------------------|-----------------------------------------|--------------------|-------------------|-----------------|----------|
| Steel Producer |                 |            |                   |                   |                                         |                    |                   |                 |          |
| 31             | Kawasaki Steel  | Chiba      | Coke Oven         |                   | 500                                     | N                  | Hitachi Ltd.      | GN <sup>a</sup> | 1976     |
| 32             | Kawasaki Steel  | Chiba      | Sintering Machine |                   | 762                                     | N                  | Hitachi Zosen     | G <sup>b</sup>  | 1977     |
| 33             | Kobe Steel      | Amagasaki  | Coke Oven         |                   | 104                                     | R                  | Kobe Steel        | GN              | 1977     |
| 34             | Nippon Kokan    | Ogishima   | Sintering Machine |                   | 1,320                                   | R                  | Nippon Kokan      | GN <sup>c</sup> | 1979     |
| 35             | Nippon Steel    | Kimizu     | Coke Oven         |                   | 133                                     | N                  | JGC               | PP              | 1978     |
| 36             | Nisshin Steel   | Amagasaki  | Boiler            | (HO) <sup>d</sup> | 19                                      | R                  | Hitachi Ltd.      | GTN             | 1977     |
| 37             | Tohshin Steel   | Himeji     | Furnace           | (HO)              | 71                                      | R                  | Hitachi Zosen     | G               | 1976     |
| Metal Producer |                 |            |                   |                   |                                         |                    |                   |                 |          |
| 38             | Nihon Seitetsu  | Katsuma    | Furnace           | (HO)              | 10                                      | R                  | Hitachi Zosen     | G               | 1976     |
| 39             | Nippon Yafin    | Kawasaki   | Boiler            | (HO)              | 15                                      | R                  | Mitsubishi Kakoki | R <sup>e</sup>  | 1976     |
| 40             | Seitetsu Kagaku | Boiler     | Boiler            | (HO)              | 15                                      | R                  | Seitetsu Kagaku   | R               | 1975     |

<sup>a</sup> Granular catalyst, moving bed.<sup>b</sup> Granular catalyst (fixed bed).<sup>c</sup> Granular iron ore is used as catalyst in moving bed.<sup>d</sup> Heavy oil.<sup>e</sup> Replaced in 1977 with ring-tube catalyst stacked regularly to achieve parallel flow.

TABLE 5-3. SCR PLANTS FOR OTHER INDUSTRIES (Larger than 10,000 Nm<sup>3</sup>/hr)

| No.   | User                | Plant Site | Gas Source    | Fuel                        | Capacity<br>(1,000 Nm <sup>3</sup> /hr) | New or<br>Retrofit | Vendor              | Catalyst        | Start Up |
|-------|---------------------|------------|---------------|-----------------------------|-----------------------------------------|--------------------|---------------------|-----------------|----------|
| 51,52 | Alto                | Chiba      | Boiler        | LPG                         | 30 x 2                                  | N                  | Mitsubishi H.I.     | G <sup>c</sup>  | 1978     |
| 53    | Ajinomoto           | Kawasaki   | Boiler        | H <sub>2</sub> <sup>a</sup> | 180                                     | R                  | Ishibawajima H.I.   | G               | 1978     |
| 54    | Asahi Glass         | Keihio     | Furnace       | H <sub>2</sub>              | 75                                      | R                  | Asahi Glass         | GM <sup>d</sup> | 1976     |
| 55    | Atomic Power Res.   |            | Boiler        |                             | 50                                      | N                  | Kawasaki H.I.       | G               | 1977     |
| 56    | Catalyst Chem.      | Wakamatsu  | Furnace       | H <sub>2</sub>              | 10                                      | R                  | JGC                 | GM              | 1976     |
| 57    | Chiyoda Kenzai      | Kaisuka    | Boiler        | H <sub>2</sub>              | 15                                      | R                  | Babcock Hitachi     | G               | 1976     |
| 58    | Chiyoda Kenzai      | Atsugi     | Boiler        | H <sub>2</sub>              | 19                                      | R                  | Ebara               | G               | 1977     |
| 59    | Dainippon Ink       | Sakai      | Boiler        | LPG                         | 30                                      | N                  | Mitsubishi H.I.     | G               | 1978     |
| 60    | Green Chemical      | Kashima    | Furnace       | LPG                         | 10                                      | N                  | Hitachi Zosen       | G               | 1974     |
| 61    | H.N. Methanol       | Sodegaura  | Reformer      | LPG                         | 200                                     | N                  | Sumitomo Chem. Eng. | G               | 1974     |
| 62    | J. National Railway | Kawasaki   | Gas Turbine   | Kerosene                    | 1,024                                   | N                  | Babcock Hitachi     | GM              | 1981     |
| 63    | Kansai Plant        | Amagasaki  | Boiler        | Kerosene                    | 16                                      | R                  | Babcock Hitachi     | G               | 1978     |
| 64    | Kawasaki H.I.       | Akashi     | Boiler        | H <sub>2</sub>              | 25                                      | R                  | Kawasaki H.I.       | G               | 1978     |
| 65    | Kurabo              | Hirahata   | Boiler        | H <sub>2</sub> O            | 30                                      | R                  | Kurabo              | GM              | 1975     |
| 66,67 | Mitsui Toatsu       | Osaka      | Reformer      | Buthane                     | 84 x 170                                | R                  | Mitsui Toatsu       | G               | 1976     |
| 68    | Nihon Ammonia       | Sodegaura  | Reformer      | LPG                         | 290                                     | N                  | Sumitomo Chem. Eng. | G               | 1975     |
| 69    | Nihon Oil & Fat     | Amagasaki  | Boiler        | LPG                         | 20                                      | N                  | Babcock Hitachi     | G               | 1978     |
| 70    | N.N. Methanol       | Sodegaura  | Reformer      | Buthane                     | 323                                     | N                  | Mitsui Toatsu       | G               | 1976     |
| 71    | Sekisui Chem.       | Sakai      | Boiler        | LPG                         | 20                                      | N                  | Mitsui Toatsu       | G               | 1980     |
| 72    | Sumitomo Chem.      | Sodegaura  | Boiler        | H <sub>2</sub>              | 30                                      | R                  | Sumitomo Chem. Eng. | G               | 1973     |
| 73    | Sumitomo Chem.      | Niihama    | Reformer      | LPG                         | 200                                     | R                  | Sumitomo Chem. Eng. | G               | 1975     |
| 74,75 | Sumitomo Chem.      | Abgasaki   | Boiler        | LPG                         | 100 x 200                               | R                  | Sumitomo Chem. Eng. | G               | 1975     |
| 76,77 | Sumitomo Chem.      | Sodegaura  | Boiler        | H <sub>2</sub>              | 250 x 350                               | R                  | Sumitomo Chem. Eng. | G               | 1976     |
| 78    | Tokyo Metropolitan  | Sunamachi  | Incinerator   | Sludge                      | 100                                     | N                  | Mitsui Eng.         | H <sup>e</sup>  | 1979     |
| 79    | Unitika             | Uji        | Diesel Engine | L <sub>2</sub> <sup>b</sup> | 70                                      | N                  | Unitika             | G               | 1978     |

<sup>a</sup>Heavy oil.<sup>b</sup>Light oil.<sup>c</sup>Granule.<sup>d</sup>Granule in moving bed.<sup>e</sup>Honeycomb.

in the flue gas along with 80-90% of  $\text{NO}_x$  and are suitable for certain gas sources which do not have ESPs.

There are 8 industrial SCR units which use parallel flow reactors. Nos. 1, 5, and 35 use a parallel passage reactor, Nos. 2 and 78 use a honeycomb catalyst, and Nos. 10, 13, and 39 use tube or ring-tube catalysts. Since parallel flow catalysts provide simple reliable operation, they are generally preferred to the moving bed reactor with a granular catalyst except for cases in which dust removal by the bed is important. A moving bed reactor may be useful for very dirty gases such as flue gas from a glass melting furnace which contains alkaline vapor or for low-temperature gas containing  $\text{SO}_x$ , which tends to deposit sodium sulfate or ammonium bisulfate on the parallel flow catalysts (Nos. 54 and 33).

Most of the SCR units have been operated without problems. However, several units have been shut down or operated intermittently due to the 1978 relaxation of the  $\text{NO}_x$  regulation and the downturn in the economy which reduced  $\text{NO}_x$  emissions made continuous operation of the SCR system unnecessary.

Unit Nos. 1, 3, 5, 76, and 77 are the only major units which have not been in use for over one year. These five units were constructed in 1975 and 1976, at an early stage in the development of SCR. Unit No. 12 has been operated intermittently. Unit Nos. 1, 3, and 12 require fuel for gas heating, and therefore have high operating costs.

Some of the catalysts produced before 1976 either were not resistant to  $\text{SO}_x$  or experienced dust plugging problems; most of the catalysts produced in 1976 or later had few poisoning or plugging problems. For example, the  $\text{Fe}_2\text{O}_3$ -based ring catalyst charged in 1976 for Unit No. 39 was not satisfactory and was replaced in 1977 with a  $\text{TiO}_2$ -based ring-tube catalyst. The latter catalyst has treated flue gas from an industrial boiler burning heavy oil (2.5% sulfur) for over 4 years without replacement (Section 5.3). The honeycomb catalyst of Unit No. 2 has been used for over 4 years without renewal (Section 5.2).

Most of the units, particularly the smaller ones, remove 90% or more of  $\text{NO}_x$  using 1.0 - 1.2 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$ . Although unreacted  $\text{NH}_3$  reaches 10 ppm in these units, an ammonium bisulfate problem is seldom encountered because the flue gas is usually discharged above 250°C. An ammonium bisulfate problem did occur in a few larger plants including Unit No. 12 (Shindaikyowa), which cools the gas below 250°C for better heat recovery. Units No. 2 and 12 recently used 0.6 - 0.7 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$  to remove 60-70% of  $\text{NO}_x$ . These units leaked  $\text{NH}_3$  below 1 ppm and did not have a bisulfate problem.

#### 5.1.2 Economics

The investment costs of seven SCR units are shown in Table 5-4. Costs are given for the SCR reactor, the initial charge of catalyst, connecting ducts, ammonia storage and injection facilities,  $\text{NO}_x$  and  $\text{NH}_3$  analyzers, and control systems (unless otherwise noted). Some of the unit costs include costs for the heat exchanger, heater, and fans for gas heating purposes.

In general, SCR units were expensive during the early stages of development in 1975 and 1976. The costs were substantially lowered in 1977 and 1978 due to technology developments and have increased slightly since 1979 due to inflation. The individual cost of Unit Nos. 1, 12, 39, and 65, which were constructed in 1975 and 1976 exceeds 13,000 yen/kWhr although these units are for existing boilers and include heating or test facilities. By contrast, the two units constructed in 1978 for new boilers (Nos. 2 and 13) cost only 1,230 and 2,640 yen/kWh, respectively. Unit No. 78, constructed in 1979, is fairly costly— 14,500 yen/kW—because it was designed to remove both  $\text{NO}_x$  and odor from an existing incinerator and has a heat exchanger, heater, and fans.

As opposed to SCR units for utility boilers, units for industrial uses treat various kinds and amounts of gas under a variety of conditions. Therefore, although the operating costs of SCR units for large new industrial boilers may be close to those for new utility boilers, the investment costs vary widely.

TABLE 5-4. INVESTMENT COSTS OF SEVEN INDUSTRIAL SCR UNITS

| No. | Owner        | Gas Source  | Capacity<br>(MW) <sup>a</sup> | NO <sub>x</sub><br>Removal<br>(%) | New or<br>Retrofit | Reactor<br>(Catalyst) | SV <sub>1</sub><br>(hr <sup>-1</sup> ) | Cost<br>(10 <sup>4</sup> yen) | Cost<br>(yen/kW)    | Year<br>Completed |
|-----|--------------|-------------|-------------------------------|-----------------------------------|--------------------|-----------------------|----------------------------------------|-------------------------------|---------------------|-------------------|
| 1   | Fuji Oil     | Boiler      | 23                            | 95                                | R                  | PP <sup>b</sup>       | 4,200                                  | 480                           | 20,870 <sup>c</sup> | 1976              |
| 2   | Fuji Oil     | Boiler      | 53                            | 80                                | N                  | HD                    | 5,220                                  | 65                            | 1,230 <sup>e</sup>  | 1978              |
| 12  | Shindaiyowa  | Boiler      | 150                           | 90                                | R                  | Granule               | 10,000                                 | 2,000                         | 13,300 <sup>f</sup> | 1975              |
| 13  | Ukushima     | Boiler      | 87                            | 85                                | N                  | Tube                  |                                        | 200                           | 2,640               | 1978              |
| 39  | Nippon Yakin | Boiler      | 5                             | 90                                | R                  | Ring Tube             | 3,900                                  | 66                            | 13,200 <sup>f</sup> | 1976              |
| 65  | Kurabo       | Boiler      | 10                            | 90                                | R                  | MB <sup>g</sup>       | 10,000                                 | 130                           | 13,000 <sup>h</sup> | 1975              |
| 78  | Tokyo Metro. | Incinerator | 33                            | 90 <sup>i</sup>                   | R                  | H                     | 4,000                                  | 480                           | 14,500 <sup>f</sup> | 1979              |

<sup>a</sup> Calculated from gas volume (300 Nm<sup>3</sup>/hr = 1 MW).<sup>b</sup> Parallel Passage Reactor.<sup>c</sup> Including Heater.<sup>d</sup> Honeycomb.<sup>e</sup> For catalyst and reactor.<sup>f</sup> Including fan, heat exchanger and heater.<sup>g</sup> Moving bed reactor.<sup>h</sup> Including test facilities.<sup>i</sup> Removes both NO<sub>x</sub> and offensive odor.



The operating costs for 8 units in 1979 are shown in Table 5-5. The costs range from 1,400 - 2,000 yen/kl oil or 0.33 - 0.46 yen/kWhr for the four units which do not require gas heating, and from 2,200 - 4,000 yen/kl or 0.49 - 0.93 yen/kWhr for the four units requiring gas heating. Unit No. 1 is the most expensive and has been shut down since 1977.

In 1981, the operation costs for SCR units may be slightly higher than those shown in Table 5-5 due to inflation. However, the application of SCR can be less expensive than the use of higher quality fuel for NO<sub>x</sub> abatement, as will be discussed in Section 5.3.

## 5.2 SODEGAURA REFINERY, FUJI OIL

### 5.2.1 Introduction

Fuji Oil's Sodegaura Refinery is located in the Keiyo Industrial Region near Chiba City and Tokyo. This area is the largest industrial region where stringent NO<sub>x</sub> and SO<sub>x</sub> regulations have been applied by the local government. The Sodegaura Refinery now has five boilers as shown in Table 5-6. The total boiler capacity was almost doubled between 1974 and 1977. During the same time period the permissible total NO<sub>x</sub> emissions from the refinery were cut almost in half, requiring extensive NO<sub>x</sub> abatement by combustion modification and SCR (Tables 5-6 through 5-9).

### 5.2.2 SCR Unit for CO Boiler

The flow sheet of the CO boiler and the SCR unit at the Sodegaura Refinery is shown in Figure 5-1. The SCR unit was constructed for the existing CO boiler by JGC Corporation using JGC's catalyst and the Shell parallel passage reactor. Since it was difficult to install the SCR reactor between the boiler and the economizer, an inline heater first was installed to heat the 250-300°C economizer outlet gas to 360-400°C. The SCR reactor then was installed downstream of the heater. The SCR unit was completed in 1976 and was operated for about 6 months with an NO<sub>x</sub> removal rate of 92-96% (Table 5-9). The pressure drop through the SCR reactor was 100-120 mm H<sub>2</sub>O.



TABLE 5-5. OPERATING COSTS OF SCR UNITS IN 1979 (Heavy Oil-Fired Boiler Including 7 Years Depreciation)

| No | Owner            | Capacity<br>(MW) | Reactor<br>(Catalyst) | NO <sub>x</sub><br>Removal<br>(%) | Cost     |            | Remarks          |
|----|------------------|------------------|-----------------------|-----------------------------------|----------|------------|------------------|
|    |                  |                  |                       |                                   | (yen/kW) | (yen/kwhr) |                  |
| 1  | Fuji Oil         | 23               | PP <sup>a</sup>       | 95                                | 4,000    | 0.93       | With gas heating |
| 2  | Fuji Oil         | 53               | H <sup>b</sup>        | 70                                | 1,400    | 0.32       |                  |
| 13 | Ukushima         | 87               | Tube                  | 85                                | 1,500    | 0.33       |                  |
| 36 | Nisshin Steel    | 6.5              | MB <sup>c</sup>       | 90                                | 2,800    | 0.65       | With gas heating |
| 39 | Nippon Yakin     | 5.0              | Ring Tube             | 90                                | 2,200    | 0.49       | With gas heating |
| 63 | Kansai Paint     | 5.3              | Ring                  | 90                                | 3,600    | 0.84       | With gas heating |
| 65 | Kurabo           | 10               | MB                    | 90                                | 2,000    | 0.46       |                  |
| 69 | Nihon Oil & Fats | 6.7              | MB                    | 90                                | 1,800    | 0.41       |                  |

<sup>a</sup>Parallel passage reactor.

<sup>b</sup>Honeycomb.

<sup>c</sup>Moving bed.

TABLE 5-6. BOILERS AND NO<sub>x</sub> ABATEMENT AT SODEGAURA REFINERY (1)

| Boiler    | Fuel    | Steam Rate<br>(ton/hr) | NO <sub>x</sub> Abatement Methods        |
|-----------|---------|------------------------|------------------------------------------|
| No. 4     | Oil     | 75                     | LNB <sup>a</sup>                         |
| No. 5     | Oil     | 160                    | LNB, TSC <sup>b</sup> , FGR <sup>c</sup> |
| No. 6     | Oil     | 160                    | LNB, TSC, FGR                            |
| No. 7     | Oil     | 160-200                | LNB, TSC, SCR                            |
| CO Boiler | CO, Oil | 45                     | SCR                                      |

<sup>a</sup>Low-NO<sub>x</sub> burner.<sup>b</sup>Two-stage combustion.<sup>c</sup>Flue gas recirculation.TABLE 5-7. PERMISSIBLE EMISSIONS OF NO<sub>x</sub> AND SO<sub>x</sub> FROM THE SODEGAURA REFINERY

|                                       | 1974 | 1975 | 1976 | Since 1977 |
|---------------------------------------|------|------|------|------------|
| NO <sub>x</sub> , Nm <sup>3</sup> /hr | 157  | 124  | 107  | 92         |
| SO <sub>x</sub> , Nm <sup>3</sup> /hr | 375  | 163  | 145  | 134        |

TABLE 5-8. VOLUME AND COMPOSITION OF FLUE GAS TO BE TREATED BY SCR AT THE SODEGAURA REFINERY

| Boiler       | Fuel     | Gas Volume<br>(Nm <sup>3</sup> /hr) | MW<br>Equivalent | NO <sub>x</sub><br>(ppm) | SO <sub>x</sub><br>(ppm) | Dust<br>(mg/Nm <sup>3</sup> ) |
|--------------|----------|-------------------------------------|------------------|--------------------------|--------------------------|-------------------------------|
| CO Boiler    | CO + Oil | 70,000                              | 23               | 160-200                  | 400-600                  | 60-70                         |
| No. 7 Boiler | Oil      | 200,000                             | 67               | 110-120                  | 200                      | 20                            |

TABLE 5-9. SCR UNITS AT THE SODEGAURA REFINERY

| Boiler    | Vendor           | Year<br>Completed | SV <sub>-1</sub><br>(hr <sup>-1</sup> ) | Inlet<br>NO <sub>x</sub> (ppm) | NH <sub>3</sub> /NO <sub>x</sub><br>Ratio <sup>x</sup> | Outlet<br>NO <sub>x</sub> (ppm) | Removal<br>(%) | Leak<br>NH <sub>3</sub> (ppm) |
|-----------|------------------|-------------------|-----------------------------------------|--------------------------------|--------------------------------------------------------|---------------------------------|----------------|-------------------------------|
| CO Boiler | JGC <sup>a</sup> | 1976              | 4,000                                   | 180                            | 1.1-1.2                                                | 8-15                            | 92-96          | 10-20                         |
| No. 7     | MHI <sup>b</sup> | 1977              | 6,400                                   | 115                            | 0.5-0.8                                                | 57-23                           | 50-80          | <1                            |

<sup>a</sup>JGC Corporation (using parallel passage reactor).<sup>b</sup>Mitsubishi Heavy Industries (using honeycomb catalyst).

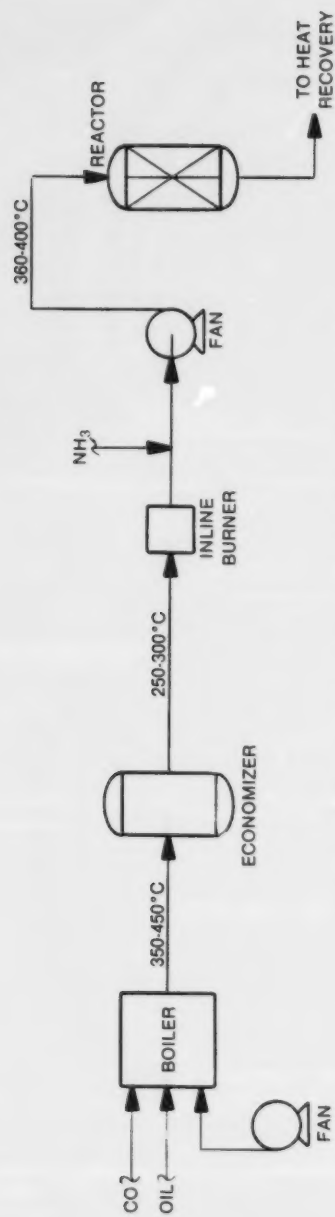


Figure 5-1 Flowsheet of CO Boiler and SCR Unit. (Fujl Oil)

Operation of the SCR unit was expensive (Table 5-5) and not energy-efficient because of the fuel requirement for gas heating as well as the high pressure drop. The SCR unit was shut down after 6 months of operation, when the operational load of the refinery dropped to 70% of capacity. At that time, total  $\text{NO}_x$  emissions were lowered to meet the standard without operating the unit.

### 5.2.3 SCR Unit for Oil-Fired Boiler

A new oil-fired boiler SCR unit was constructed in 1978 by MHI. The unit uses a NGK honeycomb catalyst and has a capacity of treating 200,000  $\text{Nm}^3/\text{hr}$  of flue gas containing about 120 ppm  $\text{NO}_x$ , 200 ppm  $\text{SO}_x$ , and 20  $\text{mg}/\text{Nm}^3$  of dust (Figure 5-2). The reactor exists in ductwork extended between the boiler and economizer and treats gas at temperatures of 330-370°C.

This SCR unit can remove about 90% of  $\text{NO}_x$  using 0.9 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$ . In order to eliminate the ammonium bisulfate problem with the economizer, the unit was operated from 1978 to 1980 with 0.7 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$ . This resulted in a  $\text{NO}_x$  reduction of nearly 70% and less than 1 ppm unreacted  $\text{NH}_3$ . Since 1980 it has operated with 0.5 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$  and obtained 50%  $\text{NO}_x$  removal with less than 1 ppm unreacted  $\text{NH}_3$ . A small amount of ammonium bisulfate still deposits on the tubes of the economizer, but the economizer can be operated without problems for more than a year at a time and is washed with water during the annual maintenance shutdown period.

After unit startup, a heavy oil additive was used for possible boiler operation improvement, and as a result a slight dust deposit was observed in the catalyst bed. The dust deposit has since been eliminated by not using the additive and applying soot blowing to the catalyst bed.

Catalytic activity tests indicated that the use of 1 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$  resulted in 93.5%  $\text{NO}_x$  removal with 5 ppm of unreacted  $\text{NH}_3$  and less than 1%  $\text{SO}_2$  oxidation during the first 2 years of operation. An 89.5%  $\text{NO}_x$

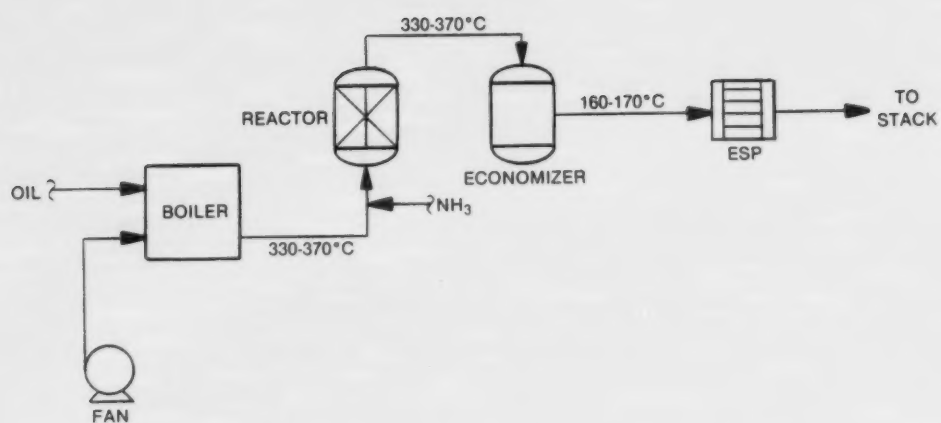


Figure 5-2 Flowsheet of Oil-Fired Boiler and SCR Unit. (Fuji Oil)

removal rate with 10 ppm unreacted  $\text{NH}_3$  and about 5%  $\text{SO}_2$  oxidation was reported after 2 years of operation. After 3-1/2 years of operation, the  $\text{NO}_x$  removal efficiency was 86.4% and the catalyst was still active.

#### 5.2.4 Evaluation

The SCR unit for the CO boiler is one of the oldest in Japan and was designed at an early stage in the development of SCR technology when fuel was still inexpensive. Today, if an SCR unit were installed on a similar boiler, the reactor might be placed between the boiler and the economizer to treat the flue gas at 350-450°C, or a low-temperature catalyst might be used for the gas leaving the economizer at 250-300°C in order to save energy.

The SCR unit for the No. 7 oil-fired boiler is one of the oldest units using a honeycomb catalyst. Both investment and operation costs are reasonable (Tables 5-4 and 5-5). Although the catalyst shows a slight decrease in activity and an increase in the  $\text{SO}_2$  oxidation ratio with time, it has been successfully used for over 4 years. The increase in the  $\text{SO}_2$  oxidation ratio may be caused by the deposition of flue gas vanadium on the catalyst. Improvements in SCR catalysts since 1978 may result in better catalysts for this type of application.

### 5.3 KAWASAKI PLANT, NIPPON YAKIN

#### 5.3.1 Introduction

Nippon Yakin is an alloy producer with a stainless steel factory in Kawasaki City adjacent to Tokyo. This area was very polluted about ten years ago and has since set stringent regulations for pollution control. The  $\text{SO}_x$  and  $\text{NO}_x$  concentrations in the factory's boiler flue gas are transmitted to the City Pollution Control Center.

The factory has 5 boilers, 2 of which use high-sulfur heavy oil (S=2.5%), while the rest use gas. Each of the 2 oil-fired boilers has a capacity of producing 6 tons of steam per hour with a total gas flow rate of about



15,000 Nm<sup>3</sup>/hr (5 MW). According to the regulation, NO<sub>x</sub> concentrations in the oil-fired flue gas must be kept below 60 ppm. Since the flue gas leaving the boiler contains about 250 ppm NO<sub>x</sub>, 1,000 ppm SO<sub>x</sub>, and about 100 mg/Nm<sup>3</sup> of dust, both SCR and FGD have been applied. To be safe, NO<sub>x</sub> is usually reduced to about 20 ppm by SCR, while SO<sub>x</sub> is reduced to 20-25 ppm by sodium scrubbing.

The other three boilers use LPG gas and maintain NO<sub>x</sub> concentrations below 50 ppm by combustion modification.

### 5.3.2 Process Description

A flowsheet of the combined SCR/FGD system used in the Kawasaki Plant is shown in Figure 5-3. Flue gas leaving the boiler at 280-300°C is heated to 330°C by a Rothemuehle heat exchanger and then to 370°C by oil-firing. After that, it is injected with ammonia, and then sent to an SCR reactor. The reactor and the heat exchanger were constructed by Mitsubishi Kakoki Kaisha (MKK) in 1976. The Sarc catalyst, a large ring-shaped catalyst based on Fe<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>, was used with a random packing during the first 6 months of operation. This resulted in a considerable increase in the pressure drop due to dust plugging, and a large decrease in catalytic activity. After 6 months the catalyst was replaced by an improved Sarc catalyst which was used for an additional 6 months without success.

In September 1977, the reactor was modified and a rashig ring type catalyst made by Catalyst and Chemicals, Inc., was charged. This catalyst has inner and outer diameters of 25 and 35 mm, a height of 40 mm, and is made of TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>. The catalyst was piled regularly to form tubes, inside and outside of which the gas passes in a parallel flow.

The new reactor went into operation in September 1977, and has operated for over four years without problems and without catalyst replacement. The volume of the catalyst is 4 m<sup>3</sup>, and the SV is 3,750 hr<sup>-1</sup>. By using 1.2 mol NH<sub>3</sub> to 1 mol NO<sub>x</sub>, 92% of the NO<sub>x</sub> is removed and unreacted NH<sub>3</sub> is kept around

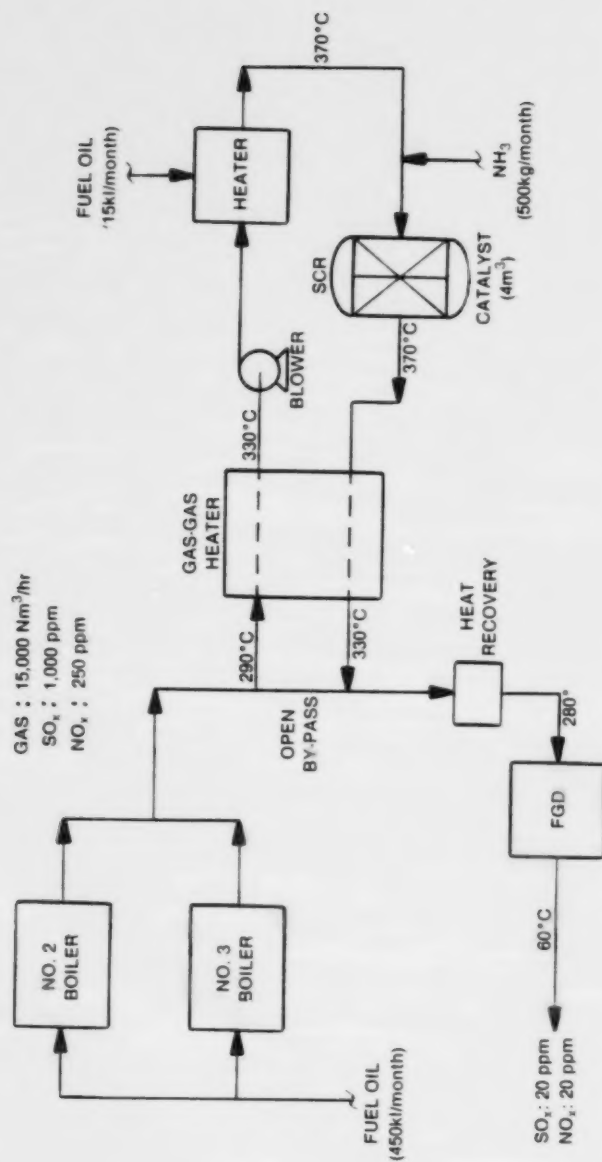


Figure 5-3 Flue Gas Treatment System at the Kawasaki Plant, Nippon Yakin.

10 ppm. The pressure drop in the reactor was 210 mm H<sub>2</sub>O at startup and increased to about 270 mm H<sub>2</sub>O after 4 years of operation. The NO<sub>x</sub> removal efficiency has remained over 90% during the 5 year period.

Flue gas leaving the SCR reactor is passed through the heat exchanger where it is cooled to 330°C. Although the gas contains considerable amounts of NH<sub>3</sub> and SO<sub>x</sub>, ammonium bisulfate does not deposit in the heat exchanger because of the high flue gas temperature. The gas is then cooled to 280°C by a heat recovery system and subjected to FGD using a spray of sodium hydroxide solution to reduce SO<sub>x</sub> to about 20 ppm. The liquor discharged from the scrubber contains sodium sulfite, sulfate, and a small amount of ammonia and is sent to a water treatment system and treated with other wastewaters from the factory.

The construction of the SCR and FGD plants required 4 months. Five days were needed to connect the plants to the boiler.

The boilers undergo a maintenance shutdown once a year. When one of the oil-fired boilers is down for maintenance, the other is in operation. Therefore, the SCR-FGD system has operated continuously for 5 years without total shutdown.

#### 5.3.3 Economics

In 1976, the Kawasaki plant's SCR system (Section 3.6) cost 73 million yen including the cost of the heat exchanger and the heater, while the FGD system cost 63 million yen. The catalyst produced by Catalyst and Chemicals, Inc. cost 6 million yen (1.5 million yen/m<sup>3</sup>) in 1977. The operating cost of the SCR and FGD systems was 30 million yen in 1979, including about 16 million yen for sodium hydroxide and 5 million yen for gas heating fuel. The 1979 annual costs are summarized below.

|                                            |  |                   |
|--------------------------------------------|--|-------------------|
| Annual cost (million yen)                  |  |                   |
| Capital cost (25% of investment)           |  | 34.0              |
| Catalyst (4 year life)                     |  | 1.5               |
| Others                                     |  | 30.0              |
| Total                                      |  | 65.5              |
| Annual Fuel Oil Consumption of the Boilers |  | 5,400 kl          |
| Annualized cost                            |  | 12,130 yen/kl oil |

In 1979, heavy oil cost 33,000 yen/kl while kerosene with the equivalent heating value cost 50,000 yen. Since the cost difference was 17,000 yen/kl, the use of heavy oil with the SCR-FGD system meant a 4,778 yen/kl saving. In 1981, heavy oil cost 50,000 yen/kl and kerosene with the equivalent heating value cost 70,000 yen while the annualized cost of the flue gas treatment system was estimated at 12,700 yen/kl. Therefore, the use of this system resulted in substantial savings.

#### 5.3.4 Evaluation

More than 4 years of continuous catalyst use may be the longest record for an SCR catalyst used to treat high sulfur oil flue gas. The smooth operation of Nippon Yakin's Kawasaki plant is a good example of the reliability of an SCR system for industrial boilers.

The catalyst used at the Kawasaki Plant was designed by Catalyst and Chemicals Inc. more than 6 years ago. Further improvements in SCR catalysts made in the past 5 years may make SCR even more reliable.

The heat exchanger has had no ammonium bisulfate problems even though the gas leaving the SCR reactor contains a considerable amount of SO<sub>2</sub> with about 10 ppm unreacted NH<sub>3</sub>, due to high gas temperatures (330°C). The gas is subsequently cooled to 280°C for heat recovery. Ammonium bisulfate will deposit when the gas is cooled to lower temperatures and reduction of unreacted NH<sub>3</sub> will be needed for additional heat recovery.

In the future, Nippon Yakin may replace the ring-tube catalyst with a tubular catalyst since the tubular type can be more easily packed.

#### 5.4 SCR FOR COKE OVEN FLUE GAS (NIPPON STEEL)

##### 5.4.1 Introduction

Nippon Steel, Japan's largest steel producer, Nippon Steel Chemical and JGC Corp. have conducted large-scale SCR tests with coke oven flue gas at Nippon Steel's Kimitsu Works Plant. The coke oven flue gas has a flow rate of 152,000 Nm<sup>3</sup>/hr and contains about 400 ppm NO<sub>x</sub>, 15 ppm SO<sub>x</sub>, and less than 35 mg/Nm<sup>3</sup> of dust. The gas temperature ranges from 170-200°C. Since gas heating to 350°C for SCR is expensive, a low-temperature catalyst developed by JGC Corp. and a parallel passage reactor, originally developed by Shell, are used.

Because ammonium bisulfate gradually deposits on the catalyst and reduces its activity, the gas is periodically (once every several days) heated to above 350°C. The heating takes place in an inline heater for a few hours in order to volatilize the deposits. The SCR unit began operation in March 1978, and has operated since that time without trouble.

##### 5.4.2 Process and Operation (3)

A flow sheet of the Nippon Steel SCR system is shown in Figure 5-4. The flue gas from the coke ovens is injected with ammonia, sent through two trains of inline heaters and SCR reactors, and finally into a stack.

Figure 5-5 shows examples of the change in NO<sub>x</sub> removal efficiencies with the heating cycle during treatment of a gas containing 50 or 200 ppm SO<sub>x</sub>. The efficiency was lowered more rapidly with gas richer in SO<sub>x</sub> due to the deposition of larger amounts of bisulfate. After being heated at 400°C for two hours, the catalyst activity returned to its original level.

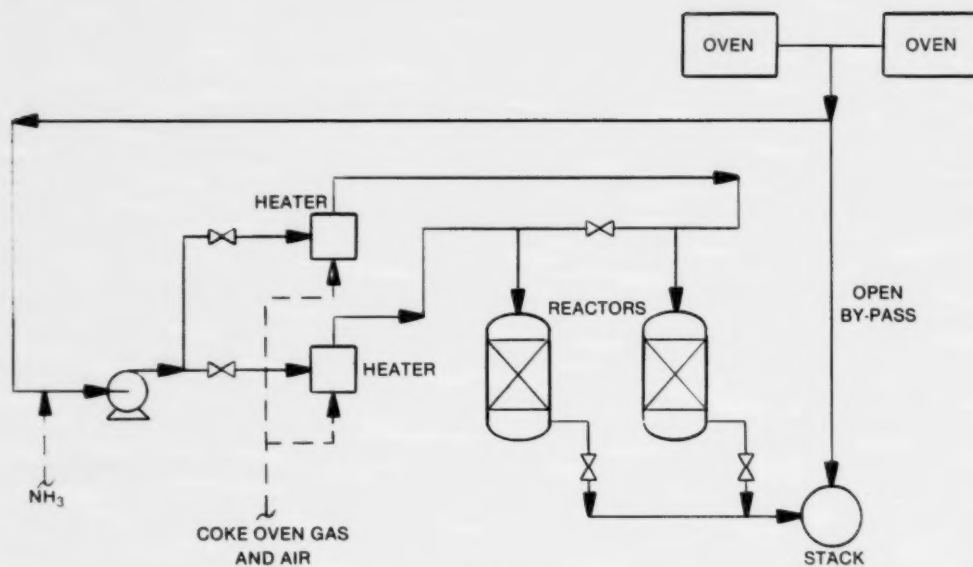
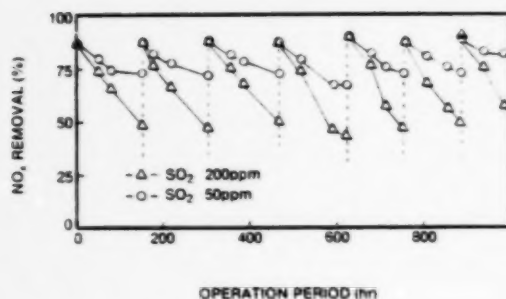


Figure 5-4 Flowsheet of an SCR System for a Coke Oven.





CATALYST: JP 501 AT 250°C  
 HEATING CONDITION: 400°C, 2 hours  
 GAS COMPOSITION: NO: 200 ppm; NH<sub>3</sub>: 220 ppm;  
 O<sub>2</sub>: 3%; H<sub>2</sub>O: 10%; N<sub>2</sub>: balance

Figure 5-5 Change in NO<sub>x</sub> Removal Efficiency During Heating Cycle. (4)

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| CONCENTRATIONS (ppm) | TYPE OF TEST                | SV<br>(hr <sup>-1</sup> ) | TEMP<br>(°C) | NH <sub>3</sub><br>NO <sub>x</sub> | NO <sub>x</sub> REMOVAL (%) |    |    |
|----------------------|-----------------------------|---------------------------|--------------|------------------------------------|-----------------------------|----|----|
|                      |                             |                           |              |                                    | 50                          | 70 | 90 |
|                      | STANDARD                    | 2,700                     | 200          | 1.3                                |                             |    | 1  |
|                      | AT 180°C                    | 3,500                     | 180          | 1.2                                |                             |    | 2  |
|                      | LOW NH <sub>3</sub> (180°C) | 3,500                     | 180          | 0.9                                |                             |    | 2  |
|                      | LESS FREQUENT HEATING       | 3,500                     | 180          | 0.9                                |                             |    | 2  |
|                      | WITHOUT HEATING             | 3,500                     | 170          | 0.9                                |                             |    | 2  |
|                      | WITHOUT HEATING             | 3,500                     | 170          | 0.7                                |                             |    | 2  |

Figure 5-8 Operating Conditions and NO<sub>x</sub> Removal Efficiency. (3)

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Tests were conducted continuously for one year from April 1978 through March 1979 under varied conditions, as shown in Table 5-10.

TABLE 5-10. NIPPON STEEL SCR SYSTEM TEST CONDITIONS

|                                             |        |      |       |     |
|---------------------------------------------|--------|------|-------|-----|
| Temperature (°C)                            | 170,   | 180, | 200   |     |
| SV (hr <sup>-1</sup> )                      | 2,700, |      | 3,500 |     |
| NH <sub>3</sub> /NO <sub>x</sub> mole ratio | 1.3,   | 1.2, | 0.9,  | 0.7 |

The NO<sub>x</sub> removal efficiencies with different operating conditions are shown in Figure 5-6. With the standard condition of 200°C with an SV of 2,700 hr<sup>-1</sup> and a mole ratio of 1.3, the NO<sub>x</sub> removal efficiency was 94-98%. The efficiency was 84-92% at 180°C with a mole ratio of 1.2 and an SV of 3,500 hr<sup>-1</sup>, and 78-88% with a mole ratio of 0.9. When gas heating to 400°C took place over longer intervals, the NO<sub>x</sub> removal efficiency was lowered. Tests were conducted using 170°C flue gas without gas heating. These tests indicated that the removal efficiency was 60-70% with a mole ratio of 0.9 and about 50% with a mole ratio of 0.7.

The NO<sub>x</sub> removal efficiency under the standard condition was 98% at the beginning and 97% at the end of the tests, which indicated that there was little, if any, degradation of the catalyst during the one-year test period. Tests also have shown that, immediately after being heated to 400°C, the catalyst produced a relatively low NO<sub>x</sub> removal efficiency for a short time period. For example, the NO<sub>x</sub> removal efficiency was about 80% with 1 mol NH<sub>3</sub> to 1 mol NO<sub>x</sub> at 180°C immediately after the heating, and increased to nearly 90% in a few hours. It appears that the catalyst absorbs more ammonia at lower temperatures than at higher temperatures. A considerable amount of ammonia is released from the catalyst when it is heated to 400°C. After being heated to 170-200°C, the catalyst absorbs ammonia in the flue gas until saturation is reached. Saturation results in a temporary shortage of ammonia which can react with NO<sub>x</sub> in the flue gas.

The pressure drop in the reactor was 40-50 mm H<sub>2</sub>O both at the beginning and the end of the test period indicating that there was no dust plugging problem.

#### 5.4.3 Evaluation

Tests of Nippon Steel's SCR unit were conducted successfully with over 90% NO<sub>x</sub> removal efficiency under the standard conditions. Neither catalyst degradation nor dust plugging was observed during the one-year test period. Although periodic gas heating to over 350°C is needed to remove ammonium bisulfate, the use of low-temperature catalysts may be less costly than the use of a standard catalyst with continuous gas heating to 350°C. Another advantage of the system is the simple thermal treatment in the fixed bed. Operation of this system is much easier than using a moving bed with a catalyst that is discharged from the reactor for NO<sub>x</sub> treatment. However, low-temperature catalysts may not be suitable for SO<sub>x</sub>-rich gas because of the requirement for frequent gas heating.

Parallel passage reactors are expensive because they use many steel gauze envelopes to hold the catalyst. On the other hand, smaller, very active catalysts can be used because less physical strength is needed in these reactors. Therefore, the reactor may be suitable for a low-temperature very active catalyst.

Although the SCR system at Kimitsu works well, it does require considerable investment costs, land space, and energy. At this time, Nippon Steel has no plans to construct a commercial plant using the system.

### 5.5 SCR USING AN IRON ORE CATALYST

#### 5.5.1 Introduction

Nippon Kokan, one of the largest steel producers in Japan, constructed a full-scale SCR unit at its Keihin Works plant. The unit has a capacity of

treating 1,320,000 Nm<sup>3</sup>/hr of flue gas from an iron-ore sintering machine using iron ore as the catalyst in a moving bed reactor.

The flue gas is first subjected to dust removal by an ESP and then FGD by ammonia scrubbing, utilizing ammonia present in the coke oven gas (5). The FGD system began operation in 1976 and has operated successfully since that time. When further gas treatment for NO<sub>x</sub> removal was requested by the local government, Nippon Kokan conducted pilot plant tests of SCR using iron ore as the catalyst (2). Based on these tests, the full-scale SCR unit was completed and began operation in 1979.

#### 5.5.2 Process Description

The flow sheet of the gas treatment system at Keikin is presented in Figure 5-7. The 150°C flue gas from the sintering machine contains about 300 ppm SO<sub>x</sub>, 200 ppm NO<sub>x</sub>, and 500 mg/Nm<sup>3</sup> of dust. It passes through an ESP, heat exchanger, and an FGD unit to remove over 90% of the SO<sub>x</sub>. The flue gas leaving the FGD unit is further cleaned by a wet ESP and then heated to 110°C by a heat exchanger. An SCR unit was installed downstream of the FGD system. The gas is heated to 380-400°C by a heat exchanger and a heater, injected with ammonia, and sent into the moving bed reactor (SV=3,500 hr<sup>-1</sup>) where 80% of the NO<sub>x</sub> is removed. One specific kind of iron ore was found to be particularly active as a catalyst.

Since the flue gas after FGD still contains small amounts of SO<sub>x</sub>, a portion of the iron ore reacts to form a powdery sulfate. The ore catalyst discharged from the reactor is screened and returned to the reactor; the iron ore fines containing sulfate are returned to the sintering machine.

The SCR unit cost 6.7 billion yen including the price of the heat exchanger and the heater.



### 5.5.3 Evaluation

The iron ore-catalyst SCR system may be best suited to flue gas treatment at steel works because iron ore is inexpensive and can be utilized for steel production after it is used as a catalyst. From this standpoint, the process is quite economical, compared with standard SCR processes for which the cost of the catalyst comprises more than half of the total investment and operation costs.

Treatment of flue gas from a sintering machine still may be fairly expensive because the gas temperature is low---about 150°C at the sintering machine outlet and even lower after wet FGD treatment---thus requiring a heat exchanger and fuel for the heater.

Use of a low-temperature catalyst might reduce the fuel requirement to some extent. JGC Corporation, with funding from the Steel Federation, conducted tests of SCR with a low-temperature catalyst for flue gas leaving a sintering machine (2). These tests were conducted at 290°C or above to avoid ammonium bisulfate deposition and thus required extensive gas heating.

The system at the Keihin Works may be one of the best solutions for treating flue gas from a sintering machine to meet stringent particulate, SO<sub>x</sub>, and NO<sub>x</sub> standards.

On the other hand, where the regulations are not very stringent, a moving bed reactor with iron ore may be the best way to treat flue gas from a sintering machine directly without an ESP. This system removes 70-80% of the dust and portions of the SO<sub>x</sub> and NO<sub>x</sub>, and requires only minimal gas heating.

## 5.6 LOW-TEMPERATURE CATALYST TESTS (KOBEL STEEL)

### 5.6.1 Introduction

Kobe Steel, one of Japan's largest steel and heavy machinery producers, has developed low-temperature SCR catalysts for 180-250°C gases containing 50-



250 ppm  $\text{NO}_x$ , and 50-1,000 ppm  $\text{SO}_x$ . These catalysts have been tested at several pilot plants; the largest test plant has a capacity of treating 100,000  $\text{Nm}^3/\text{hr}$  of flue gas.

Kobe Steel's low temperature catalysts are based on  $\alpha\text{-Al}_2\text{O}_3$  or  $\text{TiO}_2$  and are characterized by containing niobium in addition to vanadium. Both pellet and honeycomb catalysts have been produced and tested. Pellet catalysts in a movable bed have been used for low temperature gases containing  $\text{SO}_x$ . Bisulfates deposit on the honeycomb catalyst which means that the catalyst frequently must be discharged from the reactor for thermal treatment.

Unlike other process developers, Kobe Steel has found that the alumina-based catalyst containing Ti, V, and Nb performs well for low temperature gas. Kobe Steel has also developed a special technique for thermally treating a catalyst to recover its initial properties.

#### 5.6.2 Catalysts and Plant Operation

The effect of niobium on the alumina-based  $\text{TiO}_2\text{-V}_2\text{O}_5$  catalyst is shown in Figure 5-8. Niobium increases  $\text{NO}_x$  removal efficiencies especially well at low temperatures. Extensive pilot plant tests have indicated that the alumina-based catalyst is superior to the titanium-based catalyst for low temperature gases. When a titanium-based catalyst was used for a 180-250°C gas containing about 50 ppm  $\text{SO}_x$  (SV:  $5,000 \text{ hr}^{-1}$ ;  $\text{NH}_3/\text{NO}_x$  mole ratio:1), the initial  $\text{NO}_x$  removal efficiency of 98% dropped to about 80% within 8-10 days of continuous operation. Although catalytic activity can be recovered when the contaminated catalyst is heated to 400-450°C, frequent heating consumes considerable energy.

When the alumina-based catalyst is used under the same conditions, the initial 90%  $\text{NO}_x$  removal efficiency drops very slowly and requires 3,000-4,000 hours to reach 80%. The large specific surface area of the alumina-based catalyst---about  $150 \text{ m}^2/\text{gram}$  compared with about  $50 \text{ m}^2/\text{gram}$  for the titania-based catalyst---may be a factor which explains the long period of

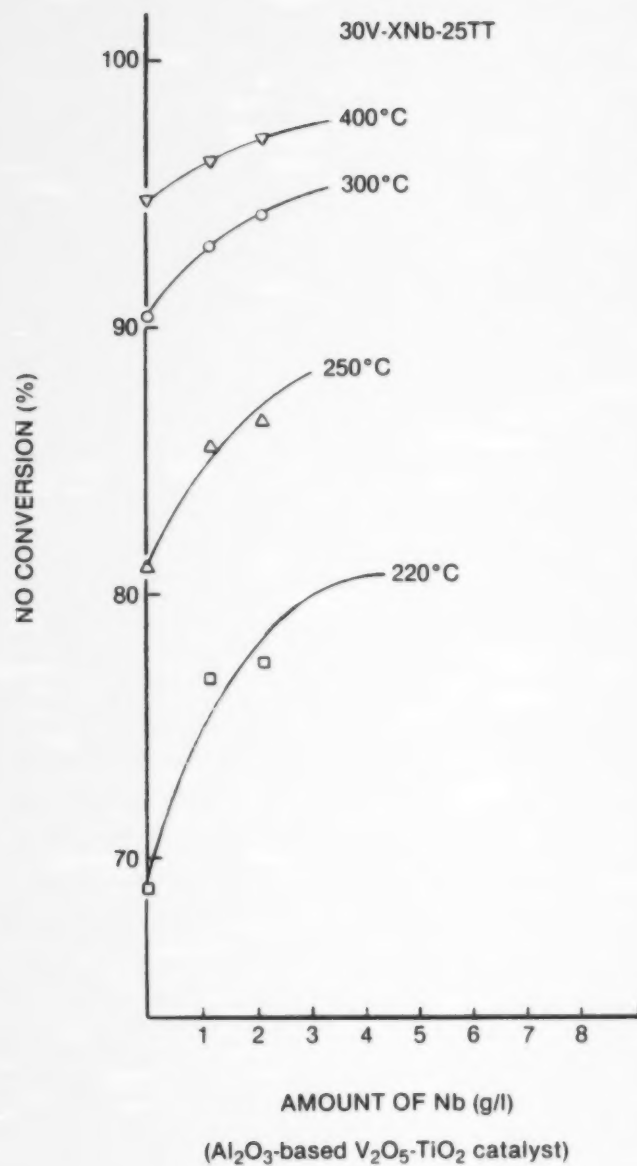


Figure 5-8 Effect of Niobium on NO<sub>x</sub> Removal.

catalyst usefulness. Another reason may be the low oxidation rate of  $\text{SO}_2$  to  $\text{SO}_3$  caused by the niobium-containing alumina-based catalyst.

Figure 5-9 shows the thermal treatment system used to treat the contaminated aluminum-based catalyst. The catalyst is heated to 550-600°C in several minutes to avoid degradation. With rapid heating for a short time, catalytic activity is restored to its original level without a loss in physical strength.

Kobe Steel's large test plant (100,000  $\text{Nm}^3/\text{hr}$ ) has been operated for over 4 years, removing 90-80% of  $\text{NO}_x$  in the 200-220°C flue gas which contains about 250 ppm  $\text{NO}_x$ , 50 ppm  $\text{SO}_x$  (including about 5 ppm of  $\text{SO}_3$ ), and 10-50  $\text{mg}/\text{Nm}^3$  of dust. Thermal treatment is applied once every 3,000-4,000 hours. The catalyst retains a sufficiently high activity and physical strength during this time. Both the catalyst and thermal treatment system have been patented in several countries including the U.S.

### 5.6.3 Evaluation

Alumina-based catalysts for SCR were popular several years ago but they are no longer used for  $\text{SO}_x$ -containing gas by most process developers and users. Instead,  $\text{SO}_x$ -resistant  $\text{TiO}_2$ -based catalysts have been developed. SCR operator experience indicates that alumina-based catalysts are often poisoned by  $\text{SO}_x$  to form aluminum sulfate when used at 300-400°C. The catalysts must be heated to 800°C in order to decompose the aluminum sulfate and recover their catalytic activity.

Kobe Steel's long-term SCR test has proved that the alumina-based catalyst is best suited to a low-temperature gas with a relatively low  $\text{SO}_x$  concentration. It appears that aluminum sulfate is not formed at lower temperatures, because ammonia in the flue gas readily combines with  $\text{SO}_3$  before the  $\text{SO}_3$  attacks the catalyst. Above 300°C, ammonia does not combine with  $\text{SO}_3$ . Thus, heating the catalyst for several minutes at 550-600°C can remove the sulfate formed on it.

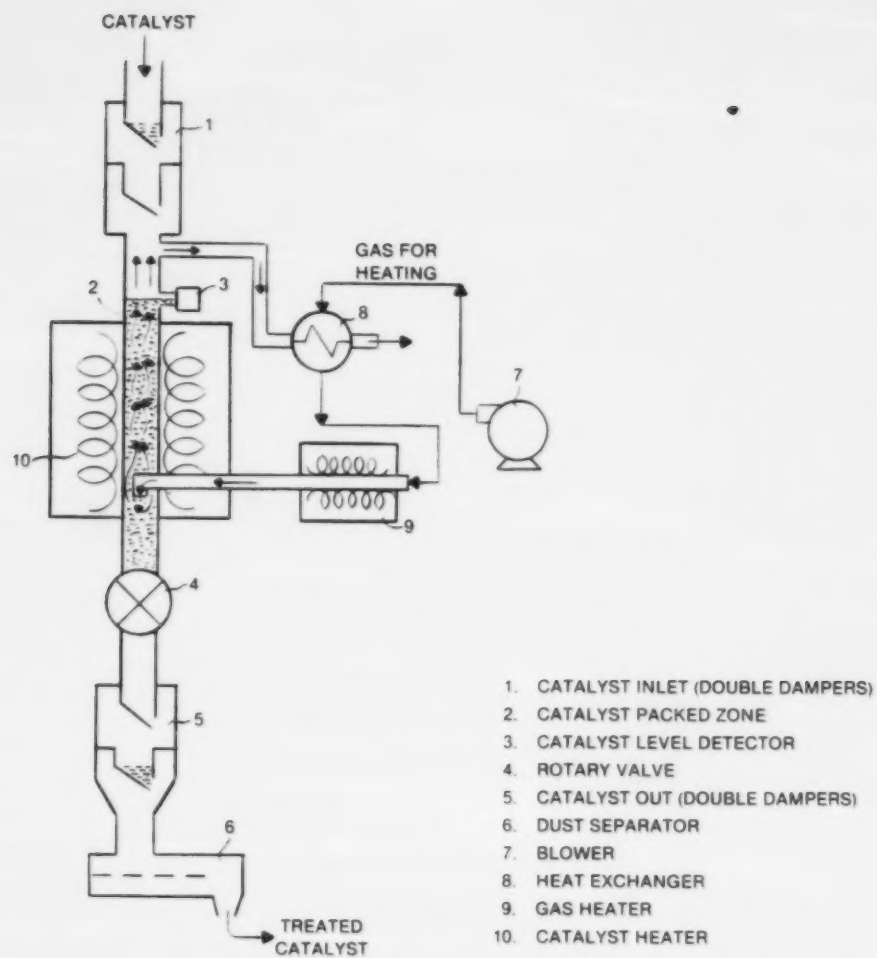


Figure 5-9 Thermal Treatment System.

Another reason for the usefulness of the alumina-based catalyst is that not much  $\text{SO}_2/\text{SO}_3$  oxidation occurs at low temperatures, although a large amount of oxidation occurs above  $300^\circ\text{C}$ . Some catalysts oxidize  $\text{SO}_2$  considerably, even at  $250^\circ\text{C}$ , which results in reduced activity (Section 3.3.2). The alumina-based catalyst containing niobium does not appear to oxidize any  $\text{SO}_2$  at  $200$ – $220^\circ\text{C}$  and yet is highly active.

The alumina-based catalyst can be used for 3,000–4,000 hours at a time and for over 4 years without degradation when used with a low-temperature gas. This amounts to a considerable energy and catalyst cost savings. The  $\text{TiO}_2$ -based catalyst produced by Kobe Steel seems to perform similarly to  $\text{TiO}_2$ -based catalysts manufactured by other producers.

When Kobe Steel's system using the alumina-based catalyst is compared with JGC's system using a  $\text{TiO}_2$ -based catalyst (Section 5.4), it can be seen that the former requires higher heating temperatures--- $550$ – $600^\circ\text{C}$  versus  $400^\circ\text{C}$ . At the same time, the energy requirement may be much less for the Kobe Steel system because of a lower required heating frequency and the fact that the catalyst is heated in a separate vessel. However, overall the Kobe Steel system is more complex than the JGC system.

Further studies are needed to demonstrate the applicability of alumina-based catalysts to gases with various compositions at various temperatures.

## 5.7 SCR FOR INCINERATOR FLUE GAS

### 5.7.1 Introduction

In Tokyo, Mitsui Engineering constructed a commercial SCR unit to remove both  $\text{NO}_x$  and odor from its sewage sludge incinerator which produces 100,000  $\text{Nm}^3/\text{hr}$  of flue gas. Prior to construction, Mitsui conducted extensive tests at the request of the Tokyo Metropolitan Government. The flue gas was found to contain over 100 ppm  $\text{NO}_x$  with considerable amounts of  $\text{SO}_x$ ,  $\text{HCl}$ , various kinds of dust, and other odorous components (including aldehydes) which are difficult to remove by carbon adsorption or wet process oxidation.



The government-owned incinerators have sodium scrubbing systems and wet ESPs for gas cleaning. The treated gas contains about 100 ppm  $\text{NO}_x$ , 5 ppm each of  $\text{SO}_x$  and  $\text{HCl}$ , and has a considerable odor. Mitsui Engineering conducted tests on flue gases both before and after gas cleaning by the scrubber and ESP. They found that a certain kind of SCR catalyst is especially useful for odor removal and applicable to the cleaned flue gas, although there are problems involved in treating the uncleaned flue gas directly. A commercial SCR unit with a capacity of treating 108,000  $\text{Nm}^3/\text{hr}$  of flue gas leaving the sodium scrubber and wet ESP subsequently was constructed; it began operation in October 1979.

#### 5.7.2 Process Description (6)

The 108,000  $\text{Nm}^3/\text{hr}$  flue gas from the incinerator contains about 100 ppm  $\text{NO}_x$ , about 5 ppm each of  $\text{SO}_x$  and  $\text{HCl}$ , less than 0.01 g/ $\text{Nm}^3$  of dust and about 10%  $\text{O}_2$ , 8%  $\text{CO}_2$ , 7%  $\text{H}_2\text{O}$ , and 75%  $\text{N}_2$  at 40–50°C. The flowsheet of the unit is shown in Figure 5-10. The flue gas is heated to 280°C in a heat exchanger and then in a heater to 350°C, injected with ammonia, and sent into a reactor containing a honeycomb catalyst at an SV of 4,000  $\text{hr}^{-1}$  and linear velocity of 7.7 m/sec. Over 90% of the  $\text{NO}_x$  and 80% of the odor are removed by using 1.1 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$ . No problems have been encountered since system start-up.

Figure 5-11 shows test results for the removal of various odorous gaseous compounds. A synthetic gas containing 10 ppm each of these compounds was sent through the SCR catalyst at different temperatures without ammonia addition. Over 90% of the compounds (except ammonia) were removed at 300°C or below, forming  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{SO}_2$  by oxidation. Tests with ammonia added to the gas indicated that ammonia did not substantially affect the removal ratio of these compounds.

#### 5.7.3 Economics (6)

The Mitsui Engineering SCR unit cost 480 million yen including the price of the heat exchanger, heater, initial catalyst charge, and civil engineering



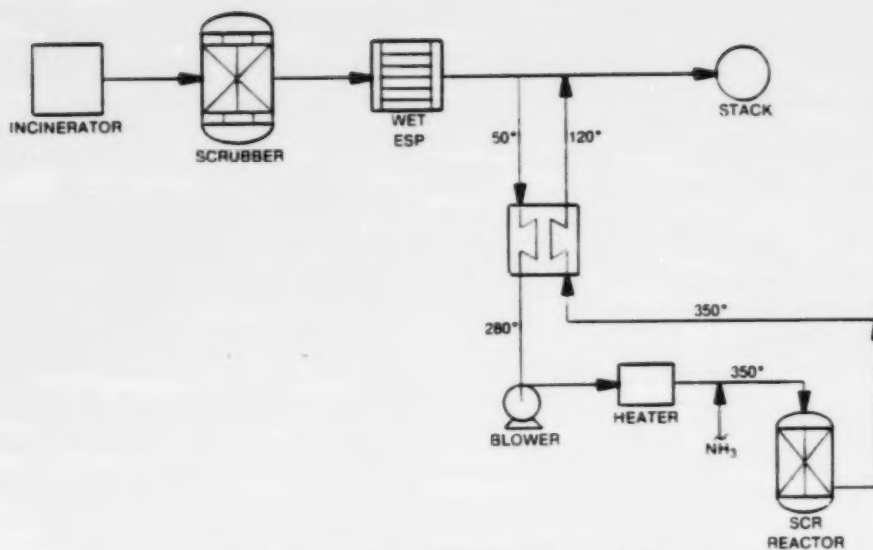


Figure 5-10 Flue Gas Treatment System for an incinerator.

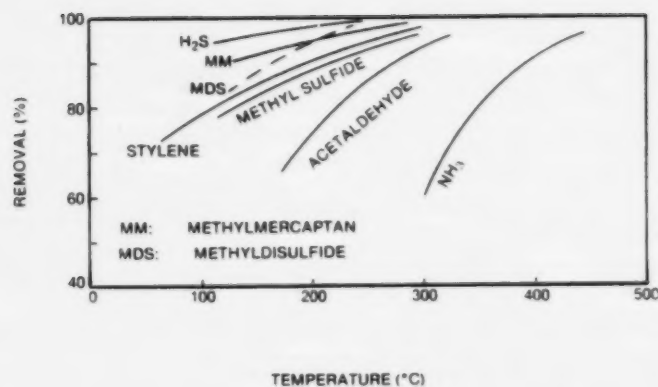


Figure 5-11 Odor Component Removal by Oxidation with the SCR Catalyst.

services. The annual cost for flue gas treatment, based on 8,000 hours of operation in 1980, is shown in Table 5-11. The total treatment cost of 450 yen/1,000 Nm<sup>3</sup> of flue gas includes the cost of kerosene for gas heating at 209 yen/1,000 Nm<sup>3</sup>. When SCR is not applied, the flue gas leaving the wet ESP must be heated. Therefore, the actual cost increase caused by the SCR unit is about 350 yen/1,000 Nm<sup>3</sup>.

#### 5.7.4 Evaluation

This SCR unit may be the first one in the world to remove NO<sub>x</sub> and odor simultaneously, and has various other NO<sub>x</sub> and odor removal applications. It is known that the presence of NO<sub>x</sub> increases the odors caused by other compounds. Therefore, NO<sub>x</sub> removal is also helpful in reducing odor. The process may be considerably less expensive when applied directly to the flue gas leaving the incinerator. Direct treatment eliminates not only the heat exchanger and the heater, but also ammonia consumption, since the flue gas usually contains ammonia sufficient for SCR.

### 5.8 OTHER SCR UNITS

#### 5.8.1 SCR Unit at Ukishima Chemical Petrochemical's Chiba Plant

For Ukishima Chemical Petrochemical, Mitsui Engineering constructed an SCR unit with a capacity of treating 260,000 Nm<sup>3</sup> of flue gas from a new oil-fired boiler. The SCR unit has a tubular catalyst with an SV of 4,000 hr<sup>-1</sup>. The unit began operation in 1978 with an investment cost of 260 million yen (2).

The 350-400°C flue gas from the boiler contains about 150 ppm NO<sub>x</sub>, 50-300 ppm SO<sub>x</sub>, and 100-150 mg/Nm<sup>3</sup> of dust. By using 1 mol NH<sub>3</sub> to 1 mol NO<sub>x</sub>, an 85% NO<sub>x</sub> removal rate has been achieved. The removal efficiency decreased slightly during the first 2 years of operation. In 1980, one-third of the catalyst was replaced with a honeycomb catalyst to maintain the high removal efficiency. Mitsui Engineering currently prefers honeycomb to tubular catalysts.

TABLE 5-1. MITSUI COST CALCULATION (MITSUI ENGINEERING)

| Conditions                     | Plant Design Capacity                    | (A) Capacity 100,000 Nm <sup>3</sup> /h                               | (B) Operation Hours 8,000 h/year        |                               |  |
|--------------------------------|------------------------------------------|-----------------------------------------------------------------------|-----------------------------------------|-------------------------------|--|
|                                | Investment Cost<br>(1,000 Yen)           | (C) Equipment 357,000<br>(D) Civil Work 48,000<br>(E) Catalyst 75,000 | (F) Total Cost 480,000                  |                               |  |
| Long Term Loan<br>(1,000 Yen)  | (G) 405,000                              |                                                                       | Interest 7%                             |                               |  |
|                                | (H) 82,925                               |                                                                       | Interest 9%                             |                               |  |
| Short Term Loan<br>(1,000 Yen) |                                          |                                                                       |                                         |                               |  |
| Variable Cost                  | Annual Quantity                          |                                                                       | Unit Price                              | Annual Expense<br>(1,000 Yen) |  |
|                                | Electricity 360 kW x (B)                 |                                                                       | kWh 14 Yen/kWh                          | 40,320                        |  |
| Utilities                      | Kerosene 380 l/h x (B)                   |                                                                       | l 55 Yen/l                              | 167,200                       |  |
|                                | Ammonia 7.6 kg/h x (B)                   |                                                                       | kg 180 Yen/kg                           | 10,944                        |  |
| Tertiary Treatment<br>Water    | 15 t/h x (B)                             |                                                                       | t 5 Yen/t                               | 600                           |  |
|                                | Catalyst 25m <sup>3</sup> /2 Years x 1.2 |                                                                       | m <sup>3</sup> 3,000 Yen/m <sup>3</sup> | 37,500                        |  |
| Consumables                    | (C) x 0.005                              |                                                                       | 1,785                                   |                               |  |
|                                |                                          |                                                                       | 258,349                                 |                               |  |
| Total Variable Cost            |                                          |                                                                       |                                         | 45,900                        |  |
| Depreciation                   | Equip.                                   | (C) x 0.9 ÷ 7                                                         | 2,160                                   |                               |  |
|                                | Civil                                    | (D) x 0.9 ÷ 20                                                        | 3,240                                   |                               |  |
| Fixed Property Tax             |                                          | [(C) + (D)] x 0.016 x 1/2                                             | 2,400                                   |                               |  |
| Insurance                      |                                          | (F) x 0.005                                                           | 7,500                                   |                               |  |
| Labor                          |                                          | 3 Men x 2,500,000 Yen Man/Year                                        | 12,150                                  |                               |  |
| Repair                         |                                          | [(C) + (D)] x 0.03                                                    | 73,350                                  |                               |  |
| Total Fixed Cost               |                                          |                                                                       |                                         | 331,699                       |  |
| Total Direct Cost              |                                          |                                                                       |                                         | 4,800                         |  |
| Overhead for Head Office       | (F) x 0.01                               |                                                                       | 16,200                                  |                               |  |
|                                |                                          |                                                                       | 7,463                                   |                               |  |
| Long Term Loan                 |                                          | (G) x 0.007 x [(7 ÷ 1) / (2 x 7)]                                     | 28,463                                  |                               |  |
| Short Term Loan                |                                          | (H) x 0.09                                                            | 360,162                                 |                               |  |
| Total Indirect Cost            |                                          |                                                                       |                                         | 450 Yen/1,000 Nm <sup>3</sup> |  |
| Total Annual Expense           |                                          |                                                                       |                                         |                               |  |
| Treatment Cost                 |                                          |                                                                       |                                         |                               |  |

### 5.8.2 Shindaikyowa Petrochemical's Yokkaichi Plant

In 1975, Hitachi Zosen constructed an SCR unit with a capacity of treating 400,000 Nm<sup>3</sup>/hr of flue gas from an oil-fired boiler at Shindaikyowa Petrochemical's Yokkaichi plant. The flue gas is treated by sodium scrubbing using the Wellman-Lord process (2).

The 55-60°C flue gas leaving the scrubber contains about 150 ppm NO<sub>x</sub>, 100 ppm SO<sub>x</sub>, and 50 mg/Nm<sup>3</sup> of particulates (including about 20 mg/Nm<sup>3</sup> of sodium salts). The gas is heated to 330-340°C by a heat exchanger, then to 400-410°C by an oil burner, injected with ammonia and sent into a reactor with a pellet catalyst. About 80% of the NO<sub>x</sub> is removed by using 1 mol NH<sub>3</sub> to 1 mol NO<sub>x</sub>, producing about 10 ppm of unreacted NH<sub>3</sub>. The treated gas is then passed through a heat exchanger where it is cooled to 160-170°C. A serious ammonium bisulfate deposit problem was encountered with the heat exchanger and frequent water washings were required.

Since the relaxation of the NO<sub>x</sub> emission regulations in 1979, 0.6-0.7 mol NH<sub>3</sub> to 1 mol NO<sub>x</sub> has been used to remove 60-70% of NO<sub>x</sub> and maintain unreacted NH<sub>3</sub> below 1 ppm. This change eliminated the previous bisulfate deposition problem.

### 5.8.3 Kawasaki Steel's Chiba Plant

In 1976, Hitachi Zosen constructed an SCR unit with a capacity of treating 762,000 Nm<sup>3</sup>/hr of flue gas from an iron ore sintering machine (2) at Kawasaki Steel's Chiba Plant. The flue gas is treated by wet lime scrubbing and wet ESP, heated by a heat exchanger and heater to 400°C, and subjected to SCR. The SCR unit has been operated without problems for 4 years. In late 1980, the catalyst was replaced, although it was still active. The new catalyst (also supplied by Hitachi Zosen) works at lower temperatures and therefore saves energy.

#### 5.8.4 SCR for Diesel Engine Flue Gas

In 1978, the Unitika Company constructed an SCR unit with a capacity of treating 70,000 Nm<sup>3</sup>/hr flue gas from a power-generation diesel engine fueled by 1.5% sulfur oil. The 350-400°C flue gas contains 900-1,100 ppm NO<sub>x</sub>, 600 ppm SO<sub>x</sub> and 100-150 mg/Nm<sup>3</sup> dust with 13% O<sub>2</sub>.

The SCR unit uses a 4 mm spherical TiO<sub>2</sub>-based catalyst in an intermittent moving bed with an SV of 10,000 hr<sup>-1</sup>. Nearly 85% of the NO<sub>x</sub> is removed using 0.85 mol NH<sub>3</sub> to 1 mol NO<sub>x</sub> and unreacted NH<sub>3</sub> is maintained at a barely detectable level. The SCR unit began operation in April 1978, and has been operated since that time without trouble. About 10% of the catalyst is replaced annually.

After SCR and heat recovery, the SO<sub>x</sub> in the gas is adsorbed by activated carbon. The carbon is washed with water to recover sulfuric acid in the same manner as has been done with the flue gas from an industrial boiler (5). Unitika conducted tests of simultaneous NO<sub>x</sub> and SO<sub>x</sub> removal by activated carbon and ammonia with thermal regeneration of SO<sub>2</sub> (2). However, the tests were discontinued when carbon consumption was found to be unacceptably high.

#### 5.8.5 SCR for Gas Turbine Flue Gas

Hitachi Ltd. and Babcock Hitachi constructed a combined-cycle power generation unit using kerosene, and an SCR unit for Japan National Railway's Kawasaki Plant. The gas and steam turbines have a capacity of 97.1 MW and 44.2 MW, respectively, with a total power generation capacity of 141.3 MW. They produce 1,024,000 Nm<sup>3</sup>/hr of flue gas. Since the flue gas temperature at the gas turbine outlet is too high for SCR, the gas is passed through one of the two boilers where it is cooled to 364°C, treated by SCR, and then sent into another boiler.

The kerosene fuel contains about 0.05 sulfur and the flue gas contains small amounts of SO<sub>x</sub> and dust with about 75 ppm NO<sub>x</sub>. A moving bed reactor with a pellet catalyst is used for SCR. The entire system was designed in



1977, when Hitachi's plate catalyst was not yet well developed. Since the system is operated about 14 hours a day with a shutdown at night, the catalyst undergoes startup heating and shutdown cooling every day. In 1977, Hitachi was not confident about the reliability of the plant catalyst under such conditions, but currently prefers the plate catalyst in a fixed bed rather than a moving bed for this type of gas.

The system began operation in April 1981, and has operated without problems since then. About 80% of the  $\text{NO}_x$  is removed by using 1 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$ , which produces unreacted  $\text{NH}_3$  at a concentration of about 10 ppm. Because the  $\text{SO}_x$  content of the gas is low, the  $\text{NH}_3$  has not caused any deposition problems in the downstream facilities.



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2. Ando, J. NO<sub>x</sub> Abatement for Stationary Sources in Japan. EPA 600/7-79-205, U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1979.
3. Mizutani, H., et al. Test Operation of SCR for Coke Oven Flue Gas. Seitetsukenkyu No. 300, 1980. (In Japanese)
4. Shiba, M. NO<sub>x</sub> Removal from Dirty Gas by Special Reactor. Nenryo Oyobi Nensho, Vol. 46, No. 9, 1979. (In Japanese)
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6. Kudo, H., et al. Dry Process Techniques for the Removal of NO<sub>x</sub> and Odor from Flue Gas of a Sewage Sludge Incinerator, Mitsui Engineering Technical Bulletin, January 1981. (In Japanese)

## Section 6

### OTHER PROCESSES FOR NO<sub>x</sub> REMOVAL

#### 6.1 CLASSIFICATION OF NO<sub>x</sub> REMOVAL PROCESSES

NO<sub>x</sub> removal processes other than selective catalytic reduction (SCR) may be grouped into two general categories: wet and dry. The processes in each category are listed in Table 6-1.

TABLE 6-1. NO<sub>x</sub> REMOVAL PROCESSES OTHER THAN SCR

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##### Dry Process

###### NO<sub>x</sub> Removal Only

- Selective noncatalytic reduction (SNR)
- Combination of SNR and SCR
- MACT in-furnace NO<sub>x</sub> removal
- Molecular sieve adsorption

###### Simultaneous NO<sub>x</sub>/SO<sub>x</sub> Removal

- Activated carbon adsorption
- Electron beam radiation
- Copper oxide absorption

##### Wet Process

###### NO<sub>x</sub> Removal Only

- Sodium scrubbing (equimolecular absorption)
- Oxidation absorption

###### Simultaneous NO<sub>x</sub> and SO<sub>x</sub> Removal

- Oxidation reduction
- Absorption using complexing agent

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Several years ago when SCR technology had serious problems and was very costly, many of these other processes were being actively tested. However,

now that SCR has been successfully applied and costs much less, some of these processes have lost their attractiveness and been abandoned.

#### 6.1.1 Dry Processes

##### NO<sub>x</sub> Removal Only

Next to SCR, selective noncatalytic reduction (SNR) has been used most widely. Several relatively large SNR units and about 20 smaller units have been constructed. SNR uses ammonia at 800-1,000°C without a catalyst to remove 30-50% of NO<sub>x</sub> (Section 6.2). To increase the NO<sub>x</sub> removal efficiency and to reduce the unreacted NH<sub>3</sub> associated with SNR, a combination of SNR and SCR using a small amount of catalyst has been tested with utility boilers (Section 6.3).

A second dry NO<sub>x</sub> removal process is MACT in-furnace reduction, in which a small amount of fuel (about 10% of total fuel) is injected above the flame to remove about 50% of NO<sub>x</sub>. Commercial application of the process has begun (Section 6.4).

A third process, molecular sieve adsorption, has been used with nitric acid plant tail gas (Section 6.9.3).

##### Simultaneous NO<sub>x</sub>/SO<sub>x</sub> Removal

The Unitika Company tested an activated carbon process to remove 80-90% of SO<sub>x</sub> and NO<sub>x</sub> simultaneously but abandoned the process because of its high carbon consumption. Tests of the activated carbon process also have been conducted by EPDC jointly with Sumitomo Heavy Industries (Section 6.5) and also by Mitsui Mining Company (Section 6.9.2).

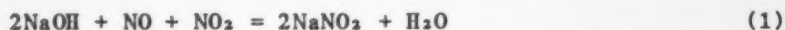
Ebara Corporation has developed an electron beam radiation process to remove 80-90% of SO<sub>x</sub> and NO<sub>x</sub> simultaneously (Section 6.6). The process is unique in that it converts SO<sub>x</sub> and NO<sub>x</sub> to ammonium sulfate and nitrate which can be used as fertilizer.

Another process, the Shell copper oxide process, has been applied to an industrial boiler where it removes about 90% of SO<sub>x</sub> and about 40% of NO<sub>x</sub> (Section 6.9.1).

#### 6.1.2 Wet Processes

##### NO<sub>x</sub> Removal Only

Essentially all of the NO<sub>x</sub> in combustion gas is in the form of NO. NO is not easily absorbed in solutions. NO<sub>2</sub> or an equimolecular mixture of NO and NO<sub>2</sub> are fairly reactive with solutions although their reactivity is less than that of SO<sub>2</sub>. The tail gas from a nitric acid plant contains both NO<sub>2</sub> and NO which can be absorbed by a sodium hydroxide solution to produce sodium nitrite by the following reaction:



This is the basis of the sodium scrubbing NO<sub>x</sub> removal process.

However, the demand for by-product nitrite is small. There are several small commercial units which first oxidize NO to NO<sub>2</sub>, then treat the gas with sodium scrubbing, and subject the resulting liquor to wastewater treatment. An oxidation absorption process such as this can not be applied on a large scale because it requires treatment of a large amount of wastewater containing nitrite and nitrate. Such treatment is very difficult.

##### Simultaneous Removal

Since 1973, many wet simultaneous removal processes have been developed. The processes can be classified into two groups: oxidation reduction and complex absorption, and are listed in Tables 6-2 and 6-3.

TABLE 6-2. OXIDATION REDUCTION PROCESSES AND PLANTS

| Process Developer  | Oxidizing Agent  | Absorbent         | By-Product                                                       | Capacity (Nm <sup>3</sup> /hr) |
|--------------------|------------------|-------------------|------------------------------------------------------------------|--------------------------------|
| Sumitomo-Fujikasui | ClO <sub>2</sub> | NaOH              | (NaNO <sub>2</sub> , NaCl, Na <sub>2</sub> SO <sub>4</sub> )     | 62,000<br>39,000<br>100,000    |
| Sumitomo-Fujikasui | ClO <sub>2</sub> | CaCO <sub>3</sub> | [Gypsum, CaCl <sub>2</sub> , Ca(NO <sub>3</sub> ) <sub>2</sub> ] | 25,000                         |
| IHI                | O <sub>3</sub>   | CaCO <sub>3</sub> | Gypsum, N <sub>2</sub>                                           | 5,000                          |
| MHI                | O <sub>3</sub>   | CaCO <sub>3</sub> | Gypsum, NH <sub>3</sub>                                          | 2,000                          |
| Chiyoda            | O <sub>3</sub>   | CaCO <sub>3</sub> | Gypsum, Ca(NO <sub>3</sub> ) <sub>2</sub>                        | 1,000                          |

TABLE 6-3. COMPLEX ABSORPTION PROCESS (USING EDTA AND FeSO<sub>4</sub>)

| Process Developer | Absorbent                               | By-Product                                      | Capacity (Nm <sup>3</sup> /hr) |
|-------------------|-----------------------------------------|-------------------------------------------------|--------------------------------|
| Chisso Eng.       | NH <sub>4</sub> OH                      | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> | 500                            |
| Asahi Chemical    | NaOH, CaCO <sub>3</sub>                 | Gypsum, N <sub>2</sub>                          | 600                            |
| Kureha Chemical   | CH <sub>3</sub> COONa CaCO <sub>3</sub> | Gypsum, N <sub>2</sub>                          | 5,000                          |
| Kureha Chemical   | KOH                                     | Sulfur, N <sub>2</sub>                          | 2,000                          |
| MKK - HZ          | KOH                                     | Sulfur, N <sub>2</sub>                          | Bench Scale                    |

Using the oxidation reduction process, NO is first oxidized by chlorine dioxide or ozone to NO<sub>2</sub>, which then is absorbed by a sodium salt solution or a calcium carbonate slurry. SO<sub>2</sub> is also absorbed to form sulfite. The NO<sub>2</sub> absorbed by the liquor is reduced by the sulfite to form N<sub>2</sub> or NH<sub>3</sub> while the sulfite is oxidized to sulfate.

The Sumitomo-Fujikasui process, which uses ClO<sub>2</sub> and sodium or limestone scrubbing, has been applied in four relatively small commercial units since 1973. However, its development has been halted because of the wastewater treatment problem associated with it (1). The similar IHI, MHI, and Chiyoda processes all use ozone to substantially reduce the wastewater treatment

problem. However, these processes are no longer being developed because of the high cost of ozone.

In order to oxidize NO to NO<sub>2</sub> economically, an NO oxidation catalyst has been studied (Section 6.8).

The complex absorption processes listed in Table 6-3 use a liquor containing EDTA and ferrous sulfate to absorb NO and form a complex compound. SO<sub>2</sub> is also absorbed to form sulfite, which in turn reduces the absorbed NO to N<sub>2</sub> or NH<sub>3</sub>. Those processes do not require an oxidizing agent but have not been commercialized because of their complexity and the requirement for a large multi-stage absorber to remove NO at a high efficiency.

#### 6.1.3 Gas Composition Appropriate for Simultaneous Removal Processes

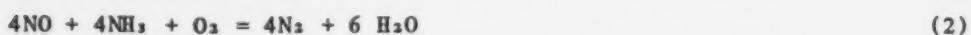
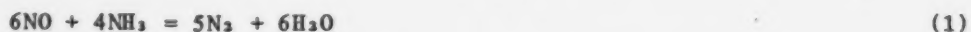
In general, a flue gas with a relatively low SO<sub>x</sub>/NO<sub>x</sub> ratio is a good candidate for dry simultaneous removal. In the electron beam process, a high SO<sub>x</sub>/NO<sub>x</sub> ratio yields a byproduct which is rich in ammonium sulfate and lean in ammonium nitrate, and is therefore a low grade fertilizer. With the copper oxide process, a high SO<sub>x</sub> content necessitates frequent regeneration of the cupric sulfate by-product and lowers the NO removal efficiency. Carbon consumption in the carbon process increases with the SO<sub>x</sub> content of the gas.

On the other hand, a high SO<sub>2</sub>/NO<sub>x</sub> ratio is preferable for the wet NO<sub>x</sub> removal processes because an excessive amount of sulfite is needed to attain a high NO<sub>x</sub> removal efficiency (1).

### 6.2 SELECTIVE NONCATALYTIC REDUCTION (SNR)

#### 6.2.1 Introduction

At about 900°C ammonia (NH<sub>3</sub>) reacts with NO<sub>x</sub> to form N<sub>2</sub> and H<sub>2</sub>O:





Selective noncatalytic reduction (SNR) is based on this reaction. During the 1970s many organizations conducted pilot plant and demonstration tests using ammonia injection (at 500-1,100°C) for NO<sub>x</sub> removal without a catalyst.

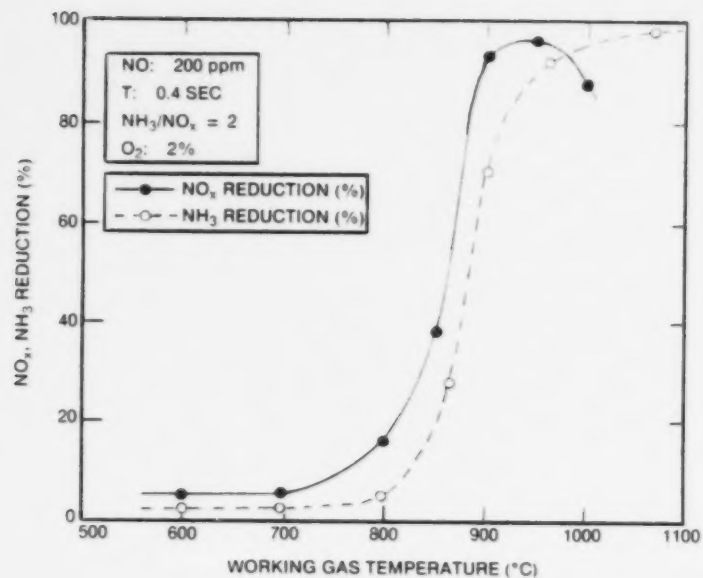
Mitsubishi Chemical Industries (MCI) and Mitsubishi Heavy Industries (MHI) conducted large-scale SNR tests using MCI's six industrial boilers. Based on the results of those tests, MHI constructed a large-scale SNR test plant for Chubu Electric at its Chita Station. The plant was designed to treat all the flue gas from a 375 MW existing oil-fired boiler. MHI also built a test plant to treat all the flue gas from an existing 375 MW oil-fired boiler at Tokyo Electric's Yokosuka Station. MCI submitted a patent application for its SNR process three months after a similar application by Exxon. Subsequently, MCI made a licensing agreement with Exxon although the patents have not been filed in Japan.

Tonen Technology also has made a licensing agreement with Exxon and has constructed 8 commercial SNR units to treat flue gases from industrial boilers and heating furnaces at oil refineries and petrochemical plants. Some of these units are specifically for use during photochemical emergency periods when more extensive NO<sub>x</sub> reduction is temporarily required (Section 6.2.5).

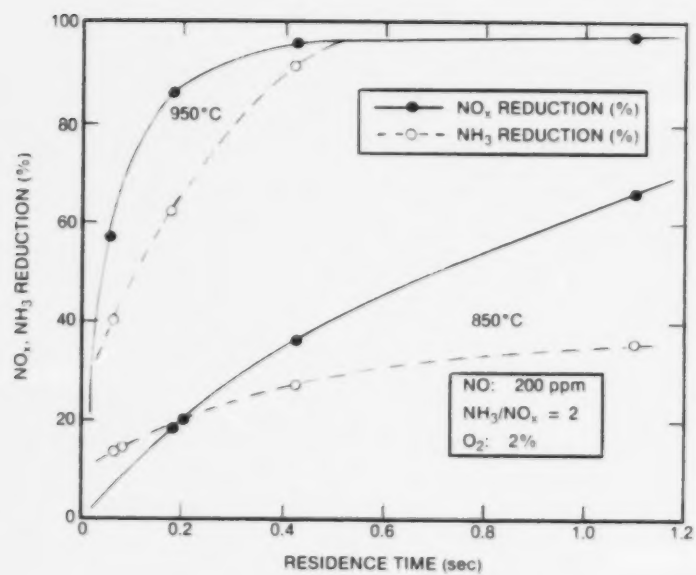
Mitsubishi Kakoki Kaisha (MKK) has developed its own SNR technology and has constructed many small commercial SNR units for a gas company (Section 6.2.6).

#### 6.2.2 MHI's SNR Laboratory Studies (2)

MHI conducted laboratory tests to determine the effects of reaction temperature and residence time (reaction time) on NO<sub>x</sub> removal efficiencies. The tests were conducted using a composite gas containing 200 ppm NO, 400 ppm NH<sub>3</sub>, and 2% O<sub>2</sub> (Figure 6-1, A, B). At temperatures between 900 and 1,000°C the reaction was at an optimum level for NO<sub>x</sub> removal and, in fact, produced a 90% NO<sub>x</sub> removal efficiency in 0.4 seconds. The principal reactions are shown in equations (1) and (2) of Table 6-4. As can be seen in Figure 6-1, B



(A) EFFECT OF WORKING GAS TEMPERATURE



(B) EFFECT OF RESIDENCE TIME

Figure 6-1 MHI Laboratory Test Data

the reaction rate was low, below 850°C. Above 1,000°C the NO<sub>x</sub> removal efficiency was lowered due to the partial conversion of NH<sub>3</sub> to NO, as shown in equation (6) of Table 6-4.

TABLE 6-4. THE MHI MECHANISM OF THE DE-NO<sub>x</sub> REACTION

| <u>Main Reaction</u>                                  |                                              |         |
|-------------------------------------------------------|----------------------------------------------|---------|
| NH <sub>3</sub> + 1/4 O <sub>2</sub>                  | ----> NH <sub>3</sub> + 1/2 H <sub>2</sub> O | Eq. (1) |
| NH <sub>3</sub> + NO                                  | ----> N <sub>2</sub> + H <sub>2</sub> O      | Eq. (2) |
| <u>Sub Reaction</u>                                   |                                              |         |
| NH <sub>3</sub> + 1/2 O <sub>2</sub>                  | ----> 1/2 N <sub>2</sub> + H <sub>2</sub> O  | Eq. (3) |
| NH <sub>3</sub> + O <sub>2</sub>                      | ----> NO + H <sub>2</sub> O                  | Eq. (4) |
| <u>Overall De-NO Reaction</u>                         |                                              |         |
| 4NO + 4NH <sub>3</sub> + O <sub>2</sub>               | ----> 4N <sub>2</sub> + 6H <sub>2</sub> O    | Eq. (5) |
| 4NH <sub>3</sub> + 5O <sub>2</sub>                    | ----> 4NO + 6H <sub>2</sub> O                | Eq. (6) |
| 4NH <sub>3</sub> + 3O <sub>2</sub>                    | ----> 2N <sub>2</sub> + 6H <sub>2</sub> O    | Eq. (7) |
| <u>Reaction Formula for NO<sub>2</sub></u>            |                                              |         |
| 2NO <sub>2</sub> + 4 NH <sub>3</sub> + O <sub>2</sub> | ----> 3N <sub>2</sub> + 6H <sub>2</sub> O    | Eq. (8) |

The NO<sub>x</sub> removal efficiency at an actual plant may be much lower than the laboratory rate due to insufficient reaction times and the difficulty involved in obtaining a rapid uniform mix of ammonia and gas. In order to study these problems, the reaction constants K<sub>1</sub>, K<sub>2</sub> and K<sub>3</sub> (as shown in Table 6-5) were determined empirically for different temperatures. This makes it possible for the NO/NH<sub>3</sub> reaction rate to be calculated using equations (12) and (13) of Table 6-5.

TABLE 6-5. BASIC FORMULAS FOR THE MHI PROCESS DE-NO<sub>x</sub> REACTION AND RATE OF REACTIONS

|                                                                                                          |                     |                                     |          |
|----------------------------------------------------------------------------------------------------------|---------------------|-------------------------------------|----------|
| 4NO + 4NH <sub>3</sub> + O <sub>2</sub>                                                                  | $\xrightarrow{K_1}$ | 4N <sub>2</sub> + 6H <sub>2</sub> O | Eq. (9)  |
| 4NH <sub>3</sub> + 5O <sub>2</sub>                                                                       | $\xrightarrow{K_2}$ | 4NO + 6H <sub>2</sub> O             | Eq. (10) |
| 4NH <sub>3</sub> + 3O <sub>2</sub>                                                                       | $\xrightarrow{K_3}$ | 2N <sub>2</sub> + 6H <sub>2</sub> O | Eq. (11) |
| $-\frac{d(NO)}{dt} = K_1[NO]^a[NH_3]^\beta[O_2]^{\gamma_1} - K_2[NH_3]^\delta[O_2]^{\gamma_2}$           |                     |                                     |          |
|                                                                                                          |                     |                                     | Eq. (12) |
| $-\frac{d(NH_3)}{dt} = K_1[NO]^a[NH_3]^\beta[O_2]^{\gamma_1} + (K_2 + K_3)[NH_3]^\delta[O_2]^{\gamma_2}$ |                     |                                     |          |
|                                                                                                          |                     |                                     | Eq. (13) |

Computer simulation programs have been developed to predict the  $\text{NO}_x$  reduction in a large furnace. As shown in Figure 6-2, a cross section of the furnace gas passage is divided into small sections which take into account the number of ammonia injection nozzles. Each section is divided into smaller subsections both crosswise and in the direction of the gas flow so that differential equations for diffusion and mixing can be solved.

The results of one computer calculation are shown in Figure 6-3. The  $\text{NO}_x$  removal efficiency is shown along the gas flow axis. In this case, ammonia is injected into the flue gas at  $1,050^\circ\text{C}$  and drives the gas temperature down to  $900^\circ\text{C}$  in 0.14 sec. over a distance of 1.8 meters. This results in an  $\text{NO}_x$  removal efficiency of more than 50 percent.

#### 6.2.3 SNR Tests at MCI's Boilers (2)

Since 1974, SNR tests have been conducted with MCI's 6 existing oil-fired boilers (Table 6-6). All of the SNR units were constructed by MHI. The No. 3 and No. 4 boilers are the largest ones, each with a capacity of 180 MW equivalent.

As shown in Figure 6-4, ammonia injection nozzles, FF, FM, and FR with cooling water tubes were placed in three locations in the No. 3 boiler and also at the boiler wall (nozzle F). Figure 6-5, A shows the relationship between boiler load and  $\text{NO}_x$  removal efficiency when 2 mol  $\text{NH}_3$ /mol  $\text{NO}_x$  is injected from each nozzle. The FM nozzle produced the highest efficiency (50%) at full load, while nozzles F and FF produced relatively high efficiencies at the lower load. As shown in the B portion of the figure, the  $\text{NO}_x$  removal efficiency reached 60% with 4 mol  $\text{NH}_3$ /1 mol  $\text{NO}_x$ .

Because the nozzles used cooling water, low-temperature corrosion occurred due to the condensation of sulfuric acid derived from the  $\text{SO}_2$  in the flue gas. As shown in Figure 6-6, the nozzles for the No. 4 boiler use boiler water for cooling and thus improve process economy and eliminate the possibility either of corrosion or of thermal damage.

TABLE 6-6. BOILERS USED FOR THE MHI APPLICATION TESTS

| Unit Name                                  | Capacity<br>(Flue Gas<br>Flow) Nm <sup>3</sup> /h | Boiler<br>Type | Fuel        | Firing | N/R | NH <sub>3</sub><br>Injection<br>Nozzle | Start<br>of<br>Tests |
|--------------------------------------------|---------------------------------------------------|----------------|-------------|--------|-----|----------------------------------------|----------------------|
| Mizushima I - #1, MCI.                     | 175,000                                           | OT             | L.S.<br>Oil | T      | R   | NCN                                    | Aug.<br>1974         |
| Mizushima I - #2, MCI.                     | 194,000                                           | OT             | L.S.<br>Oil | T      | R   | BWN                                    | Apr.<br>1977         |
| Mizushima I - #3, MCI.                     | 540,000                                           | OT             | H.S.<br>Oil | T      | R   | BWN                                    | June<br>1975         |
| Mizushima I - #4, MCI.                     | 540,000                                           | OT             | H.S.<br>Oil | T      | R   | BWN                                    | Oct.<br>1974         |
| Yokkaichi #1, MCI.                         | 200,000                                           | OT             | H.S.<br>Oil | T      | R   | SCN                                    | May<br>1976          |
| Yokkaichi, YD Boiler,<br>MCI.              | 40,000                                            | NC             | H.S.<br>Oil | H      | R   | SCN                                    | Sept.<br>1975        |
| Chita #2, Chubu<br>Electric                | 1,000,000<br>(Unit Capacity<br>350 MW)            | CC             | L.S.<br>Oil | H      | R   | BWN                                    | Feb.<br>1976         |
| Yokosuka #4 <sup>a</sup><br>Tokyo Electric | 1,000,000<br>(Unit Capacity<br>350 MW)            | CC             | L.S.<br>Oil | H      | R   | BWN                                    | March<br>1978        |

<sup>a</sup>The Yokosuka plant uses also a catalyst (Section 6.3).

Remarks: Boiler Type: NC - Natural circulation  
CC - Controlled circulation  
OT - Once-through

Firing: T - Tangential, H - Horizontal

N/R: N - New unit, R - Retrofit

NH<sub>3</sub> Injection Nozzle:

BWN - Box-type water cooled nozzle

SCN - Steam cooled nozzle

NCN - Non-cooled nozzle

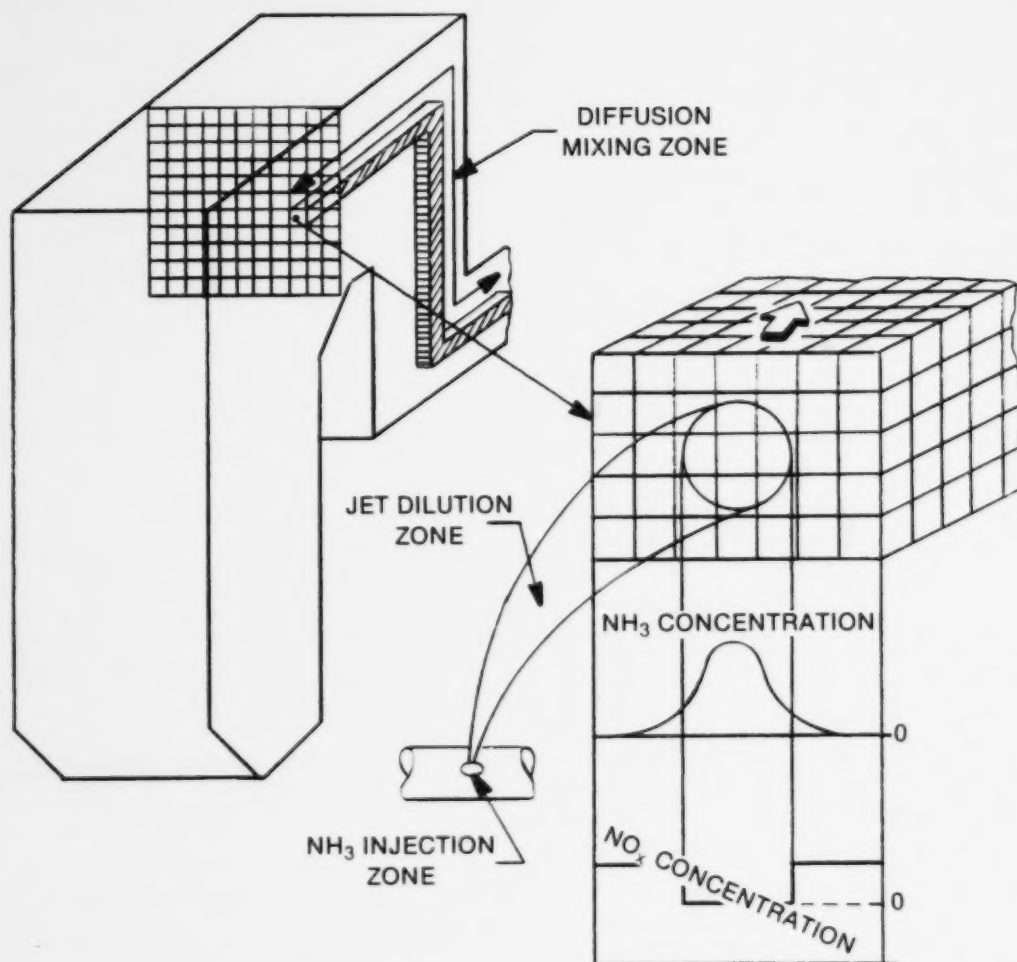


**Figure 6-2** Calculation Procedure Used in the MHI Simulation Program.



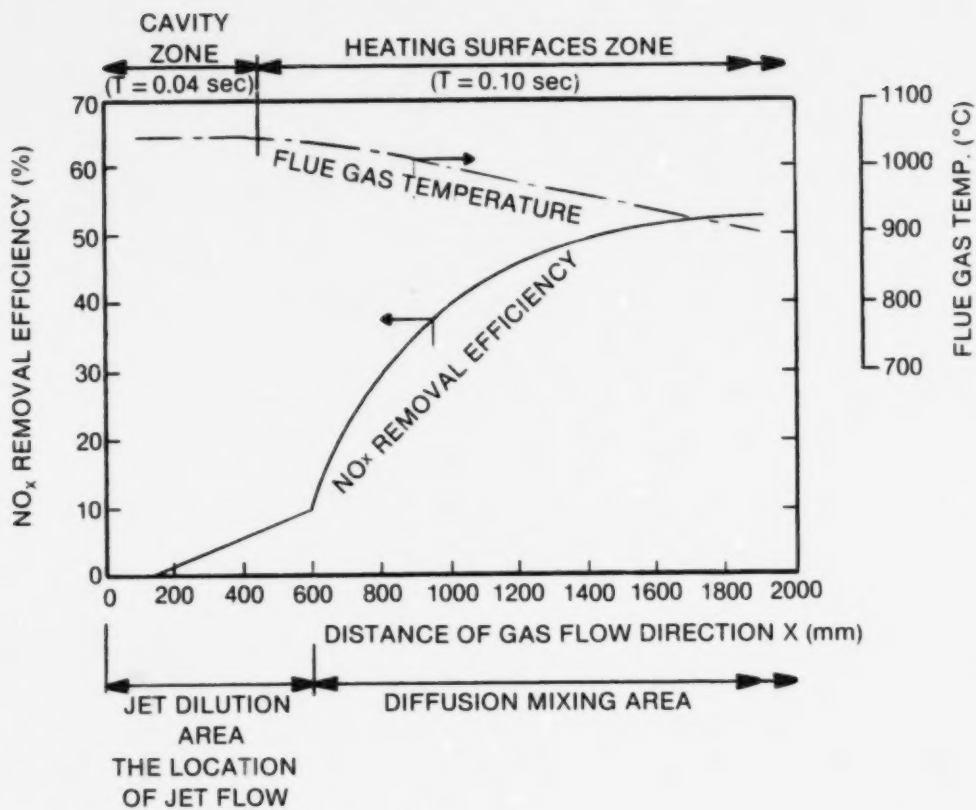


Figure 6-3 Results of a Computer Simulation of SNR DE-NO<sub>x</sub> Performance.

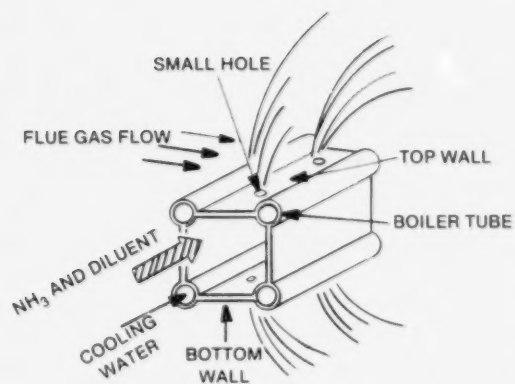
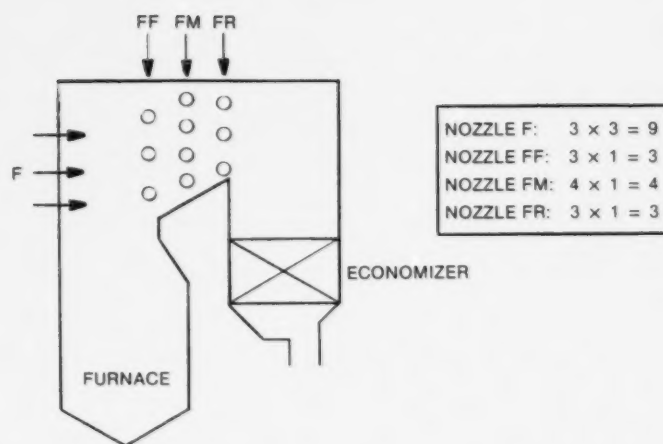


Figure 6-4 Ammonia Injection Nozzles for Mizushima Plant, Unit No. 3.

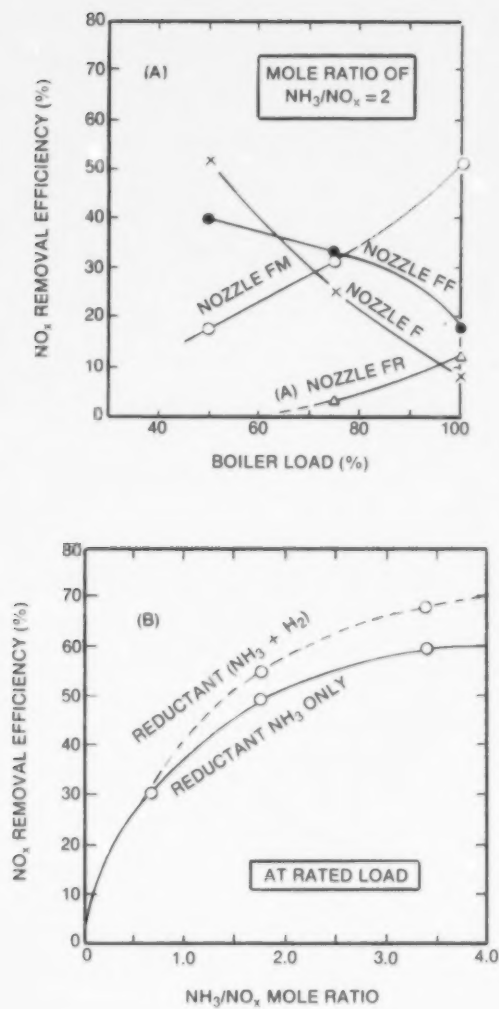


Figure 6-5 Test Results for Mizushima Plant's Unit No. 3

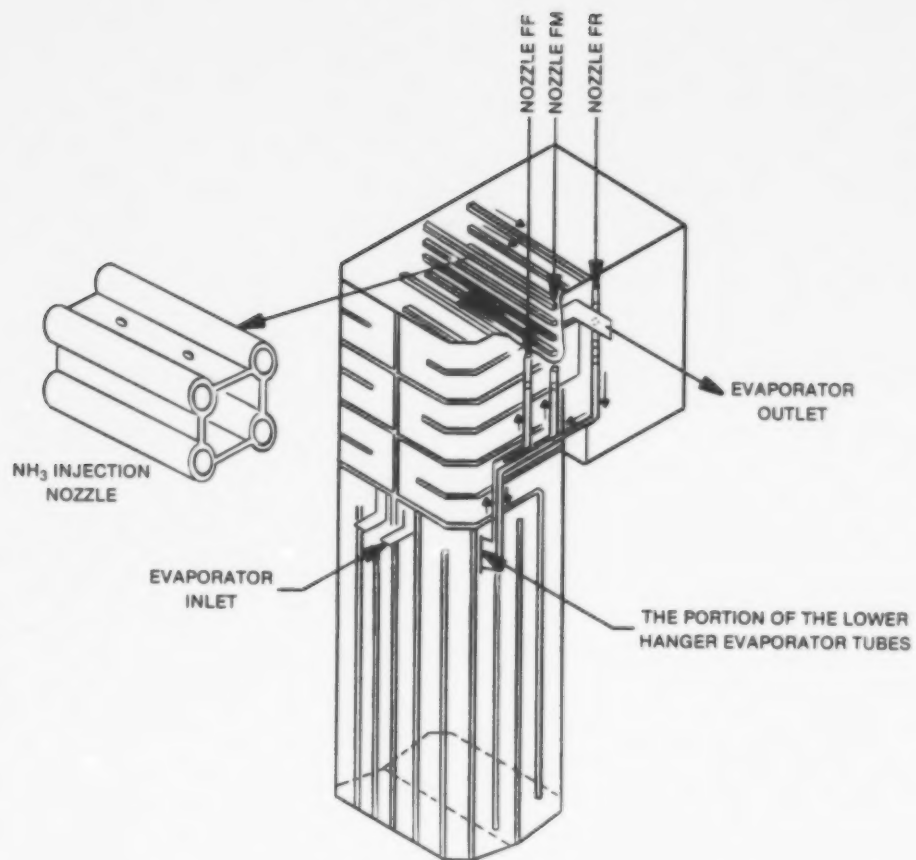


Figure 6-6 MHI Nozzle Cooling System for Unit No. 4, Mizushima Plant.

70A2832

#### 6.2.4 Full-Scale SNR Test Unit at Chubu Electric's Chita Station (2,3)

##### Boiler and SNR Unit

In 1976, Chubu Electric installed a full-scale SNR test unit for the existing No. 2 boiler at the Chita Station. The No. 2 boiler has a capacity of 375 MW and burns 0.2% sulfur oil. Among the four boilers which existed at Chita, the No. 2 boiler was chosen as being the most suited for SNR; it had space available for ammonia injection nozzles with adequate temperature ranges.

The specifications of the Chita SNR system are presented in Table 6-7. Since the boiler load fluctuates between 375 and 120 MW, a total of 15 nozzles were placed in two locations, front and rear, as shown in Figure 6-7.

TABLE 6-7. SNR SYSTEM SPECIFICATIONS, UNIT NO. 2, CHITA STATION, CHUBU ELECTRIC POWER COMPANY

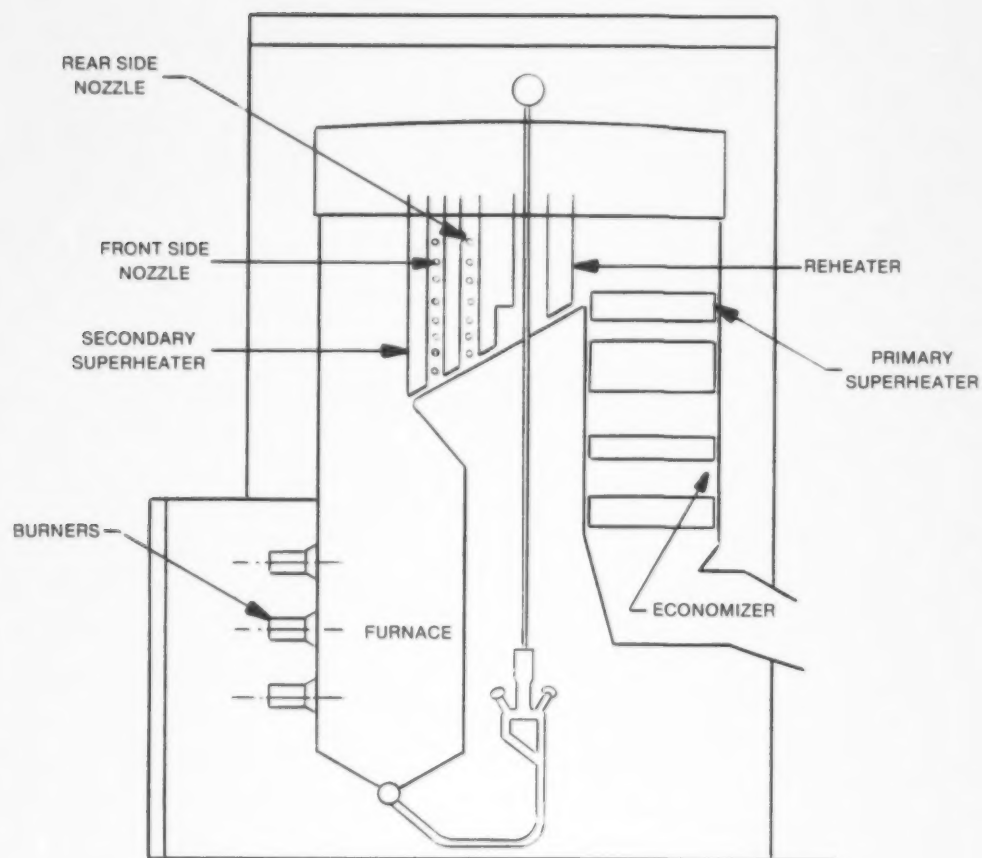
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|                                                               |                                             |
|---------------------------------------------------------------|---------------------------------------------|
| BOILER:                                                       |                                             |
| Unit Name                                                     | Unit No. 2 of Chita Station, Chubu Electric |
| Evaporation, t/h                                              | 1,225                                       |
| Steam Pressure, kg/cm <sup>2</sup> G                          | 176                                         |
| Steam Temperature, °C                                         | 571/541                                     |
| SNR TEST FACILITY:                                            |                                             |
| Treated Gas Flow Rate, Nm <sup>3</sup> /h                     | 1,000,000 (375 MW rating)                   |
| Retrofit Period                                               | Aug. 1976 ~ Jan. 1977                       |
| NH <sub>3</sub> Injection Nozzle<br>(Fin-welded box type)     | 15 sets                                     |
| Booster Air Fan for NH <sub>3</sub><br>dilution and transport | 1 set                                       |
| NH <sub>3</sub> storage and supply                            | 1 set                                       |
| SNR APPLICATION TEST START                                    | Feb. 1977                                   |
| PREDICTED DE-NO <sub>x</sub> PERFORMANCE:                     |                                             |
| Target NO <sub>x</sub> Removal<br>Efficiency, %               | 40                                          |

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★ Boiler Type: Mitsubishi-CE Control, Radiant Reheat Divided  
 Evaporation: 1225 t/h, 375 MW  
 Pressure: 176 atg  
 Temperature: 571/540.6°C

Figure 6-7 Locations of Nozzles in the No. 2 Boiler, Chita Station. ★



As shown in Figure 6-8, the rear nozzles (injection point 2) are used when the boiler load exceeds 290 MW, the front nozzles (point 1) are used with a boiler load below 220 MW, and both sets of nozzles are used with a load of between 220 and 290 MW. In this way, ammonia is always injected into the gas within a suitable temperature range--930-1,030°C. When the boiler load goes below 180 MW, ammonia injection is stopped. At this load level, the amount of  $\text{NO}_x$  produced is low enough to meet the regulations without control measures.

The SNR unit has operated almost continuously since February 1977 except for a period when the boiler was shut down. Figure 6-9 indicates the performance of the SNR system. By using 1.5 mol  $\text{NH}_3$ /1 mol  $\text{NO}_x$ , 35-45% of  $\text{NO}_x$  is removed with 15-25 ppm of unreacted  $\text{NH}_3$ . With a higher inlet  $\text{NO}_x$  concentration (about 150 ppm) the SNR unit produces a higher removal efficiency (45%). When the nozzles were modified to have more holes the result was better utilization of  $\text{NH}_3$ . The same  $\text{NO}_x$  removal rate was obtained using 1.3 mol  $\text{NH}_3$  with nozzle modification and 1.5 mol  $\text{NH}_3$  without the modification. Recently at the plant about 1 mol  $\text{NH}_3$  has been used to produce about 35% efficiency with 10 ppm unreacted  $\text{NH}_3$ .

#### Evaluation/Economics

The operation of the SNR system at Chita Station has been virtually trouble-free except for problems associated with  $\text{SO}_x$  and  $\text{NH}_3$  in the treated flue gas. The boiler flue gas contains about 100 ppm  $\text{SO}_2$  and 1-2 ppm  $\text{SO}_3$  which tend to combine with  $\text{NH}_3$  and condense on cooling. This produces 2 problems. First, during the winter, when unreacted  $\text{NH}_3$  exceeded 40 ppm, a plume was observed coming from the stack. Second, when the system began operation the pressure of the air preheater soot blower was too low. As a result, deposits in the preheater caused the pressure drop to increase from 100 to 140 mm  $\text{H}_2\text{O}$  in two months. Eventually, the boiler had to be shut down for washing of the preheater. The deposition has been reduced by using high-pressure soot blowing and less  $\text{NH}_3$  to reduce unreacted  $\text{NH}_3$ .

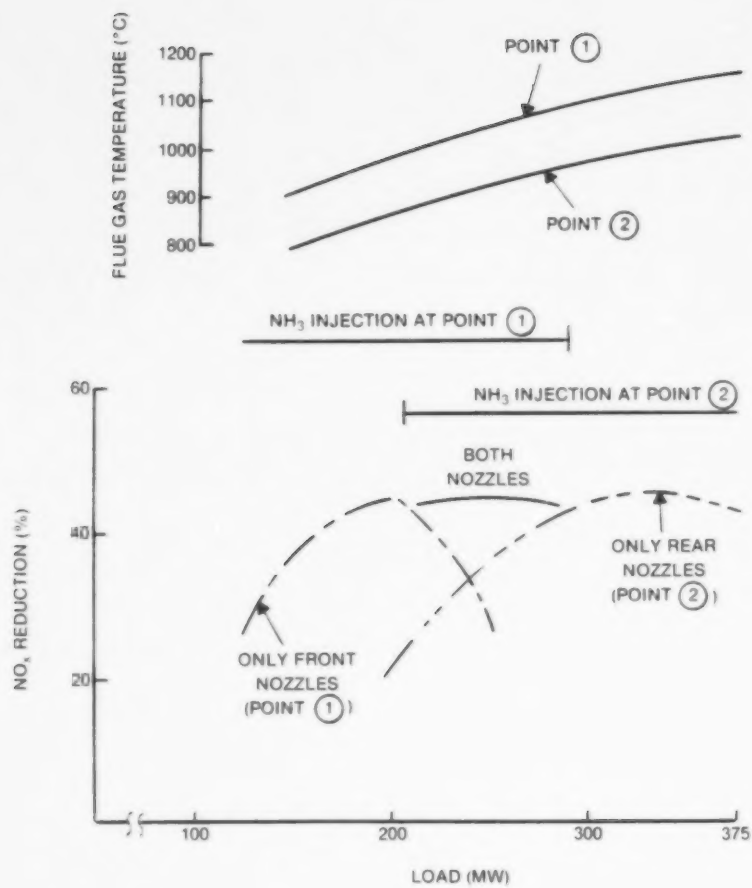


Figure 5-8 Effects of NH<sub>3</sub> Injection Position and Load on NO<sub>x</sub> Reduction Rates During Operation of the No. 2 Boiler at the Chita Station.

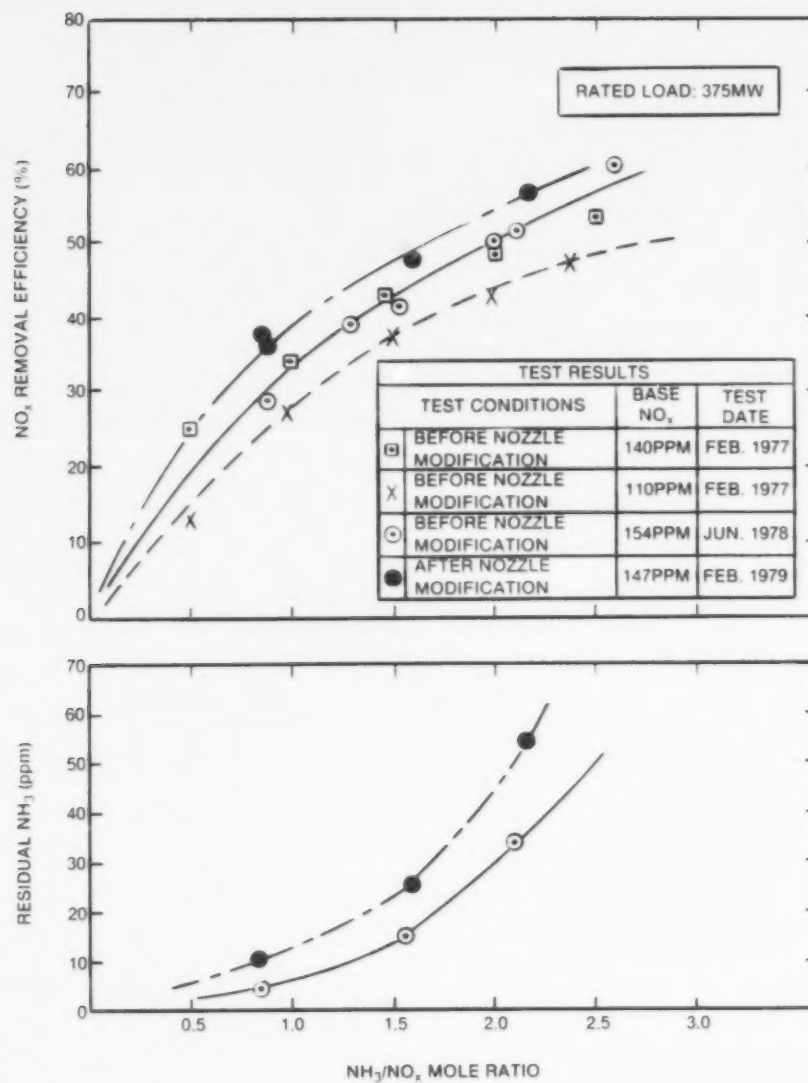


Figure 6-9 De-NO<sub>x</sub> Performance Test Results for Unit No.2 at the Chita Station.

The SNR unit cost 600 million yen (1,600 yen/kW) in 1976. This cost is quite high due to the price of boiler modification for retrofitting of the SNR unit. In general, both the costs and the  $\text{NO}_x$  removal efficiency of SNR are slightly less than half of those for SCR.

#### 6.2.5 Exxon Thermal De $\text{NO}_x$ Systems

Eight thermal De $\text{NO}_x$  SNR systems which use the technology developed by Exxon (Table 6-8) have been constructed at oil refineries and petrochemical plants. In most of the boilers and furnaces there was available space in which to install the ammonia injection nozzles at the optimum temperature of 900-1,000°C. The exception is at Mitsui Petrochemical's industrial boiler at Chiba. There the nozzles were installed where the temperature is 700-800°C and hydrogen is used with ammonia to increase  $\text{NO}_x$  removal efficiency. The ammonia and hydrogen are diluted with steam; air cannot be used for dilution because of the risk of explosion.

Mitsui Petrochemical's SNR unit has nozzles in three locations where the temperature is between 700 and 800°C. Two mol  $\text{NH}_3$  and 1-2 mol  $\text{H}_2$  to 1 mol  $\text{NO}_x$  are injected from the three locations according to the boiler load. As such, the unit removes 30-45% of inlet  $\text{NO}_x$  (100-150 ppm) with 10-15 ppm of unreacted  $\text{NH}_3$ . When the unit began operation in late 1975, the boiler burned 0.8% sulfur fuel oil and the air preheater became clogged with deposits in about 700 hours. Since then either gas or cracked naphtha fuel containing 0.2% sulfur has been used to reduce the deposition. The unit was operated for about a year and then shut down for the following reasons: 1) low  $\text{NO}_x$  removal efficiency with high unreacted  $\text{NH}_3$ , 2) high consumption of  $\text{NH}_3$  and  $\text{H}_2$ , and 3) the fact that combustion modification can reduce  $\text{NO}_x$  for a lower cost.

Tonen Sekiyu Kagaku (Tonen Petrochemical) and Toa Nenryo each operate two SNR systems (at Kawasaki and Wakayama, respectively) which meet current regulations and remove 10-20% of  $\text{NO}_x$  using 0.3-0.5 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$ . Unreacted  $\text{NH}_3$  has been maintained at 5 ppm in all four units. The regulated  $\text{NO}_x$  limit is about 140 ppm at Kawasaki and 190 ppm at Wakayama.

TABLE 6-8. EXXON TECHNOLOGY THERMAL DEMO PLANTS

| User                 | Plant Site | Gas Source        | Fuel           | Gas Treated (Nm <sup>3</sup> /hr) | Inlet NO <sub>x</sub> (ppm) | NH <sub>3</sub> /NO mole ratio | Use of H <sub>2</sub> | Gas temp. (°C) | NO removal (%) | Date of Start operation | Status of operation since 1977 |
|----------------------|------------|-------------------|----------------|-----------------------------------|-----------------------------|--------------------------------|-----------------------|----------------|----------------|-------------------------|--------------------------------|
| Mitsui Petrochemical | Chiba      | Industrial boiler | Naphtha        | 120,000                           | 130                         | 1-2 <sup>a</sup>               | Yes                   | 700-800        | 30-40          | Dec. 1973               | No operation since 1977        |
| Tonen Setiyo Kagaku  | Kawasaki   | Industrial boiler | Low-S oil, Gas | 468,000                           | ~150                        | 0.3-1 <sup>b</sup>             | Yes <sup>c</sup>      | 700-1000       | 10-50          | Oct. 1976               | Occasional                     |
| Tonen Setiyo Kagaku  | Kawasaki   | Industrial boiler | Low-S oil, Gas | 468,000                           | ~150                        | 0.3-1 <sup>b</sup>             | Yes <sup>c</sup>      | 700-1000       | 10-50          | July 1977               | Occasional                     |
| Kyokyo Petroleum     | Chiba      | Pipestill furnace | Low-S oil, Gas | 160,000                           | 80-100                      | 2.0 <sup>b</sup>               | Yes <sup>c</sup>      | 700-1000       | 50             | Oct. 1977               | For emergency                  |
| Toa Nenryo           | Kawasaki   | CO boiler         | CO             | 314,000                           | 200                         | 1-2 <sup>b</sup>               | Yes                   | 700-1000       | 45-55          | March 1978              | For emergency                  |
| Toa Nenryo           | Kawasaki   | Pipestill furnace | Low-S oil, Gas | 254,000                           | 135                         | 1-2 <sup>b</sup>               | Yes <sup>c</sup>      | 700-1000       | 50-55          | March 1978              | For emergency                  |
| Toa Nenryo           | Wakayama   | Industrial boiler | Low-S oil      | 176,000                           | ~200                        | 0.3-0.5 <sup>b</sup>           | No                    | 850-900        | 10-20          | Aug. 1978               | Continuous                     |
| Toa Nenryo           | Wakayama   | Industrial boiler | Low-S oil      | 176,000                           | ~200                        | 0.3-0.5 <sup>b</sup>           | No                    | 850-900        | 10-20          | Feb. 1981               | Continuous                     |

<sup>a</sup> NH<sub>3</sub> is injected at three locations.<sup>b</sup> NH<sub>3</sub> is injected at one location.<sup>c</sup> H<sub>2</sub> is used at about 800°C or below.

The 3 other SNR units listed in Table 6-8 have been used for emergency purposes when total  $\text{NO}_x$  emissions from the plants exceed the regulation or when photochemical smog warnings require further  $\text{NO}_x$  reduction. The units each remove 45-55% of  $\text{NO}_x$  using hydrogen and 1-2  $\text{NH}_3/\text{mol NO}_x$ .

### Economics

Tonen Technology calculated the typical cost figures for an SNR system applied to an existing boiler and furnace; these are presented in Table 6-9.

TABLE 6-9. THERMAL  $\text{DeNO}_x$  COST FIGURES CALCULATED BY TONEN TECHNOLOGY

|                                                             | Boiler         | Furnace       |
|-------------------------------------------------------------|----------------|---------------|
| Flue gas volume, $\text{Nm}^3/\text{hr}$<br>(MW equivalent) | 500,000<br>165 | 200,000<br>65 |
| Inlet $\text{NO}_x$ , ppm                                   | 200            | 200           |
| Outlet $\text{NO}_x$ , ppm                                  | 100            | 100           |
| Investment cost ( $10^6$ yen),                              | 80             | 90            |
| Utility consumption                                         |                |               |
| $\text{NH}_3$ , kg/hr                                       | 80-120         | 30-45         |
| Steam, t/hr <sup>a</sup>                                    | 2.5-3.0        | 1.0-1.2       |
| $\text{H}_2$ , $\text{Nm}^3/\text{hr}$ <sup>b</sup>         | 0-80           | 0-40          |

<sup>a</sup>Air may be used when  $\text{H}_2$  is not used.

<sup>b</sup> $\text{H}_2$  is used when the gas temperature is below  $850^\circ\text{C}$ .  $\text{H}_2$  costs 10-20 yen/ $\text{Nm}^3$ .

The investment cost may be less for a new boiler and furnace. Most of the cost of SNR systems for existing boilers and furnaces is for retrofitting. These modifications differ considerably with each boiler and furnace. Mitsui Petrochemical's SNR unit cost 140 million yen in 1975, including the cost of



the NO<sub>x</sub> analyzer, and control system and royalty fees. The cost is equivalent to 3,500 yen/kW (\$14/kW) and is fairly high due mainly to the installation of nozzles in 3 locations. The annual operating cost of the same unit was 150 million yen including 7 years depreciation, interest, overhead, and other similar costs. The annualized cost was 0.5 yen/kWhr.

#### 6.2.6 Toho Gas Company's SNR Units (4)

MKK constructed many small commercial SNR units for the Toho Gas Company at the Sorami and Chita plants near Nagoya City (Table 6-10). The units are for kerosene-fired boilers, naphtha-fired naphtha evaporation furnaces, and steam naphtha superheaters and each has a unit capacity of treating 3,200 - 10,700 Nm<sup>3</sup>/hr of flue gas.

The NO<sub>x</sub> removal efficiencies of these units are relatively high and range from 54 to 62 percent for the boilers, 58 to 67 percent for the evaporators, and 44 to 56 percent for the superheaters. No other information regarding their operation is available.

It is presumed that the inlet NO<sub>x</sub> concentrations are in the range of 100-200 ppm, and that the relatively high removal efficiencies may be due to the following: 1) the units' small size which enables rapid and uniform mixing of ammonia, 2) a relatively long reaction time in a suitable temperature range, in the case of the naphtha evaporator, 3) possible use of a large NH<sub>3</sub>/NO<sub>x</sub> mole ratio (2.0 or more), and 4) no ammonium bisulfate problem even with a large concentration of unreacted NH<sub>3</sub>, since the fuel contains little sulfur.

#### 6.2.7 Evaluation

SNR is the simplest method of flue gas treatment for NO<sub>x</sub> abatement and is well suited to boilers and furnaces which require up to 50% NO<sub>x</sub> reduction. In order to remove NO<sub>x</sub> efficiently, ammonia must be mixed with the flue gas very rapidly and uniformly. The mixed gas then should be maintained for a certain time period, preferably more than 0.2 seconds, within a suitable

TABLE 6-10. TOHO GAS COMPANY'S SNR UNITS

| Plant site | Gas Source       | Fuel      | Gas treated (Nm <sup>3</sup> /hr) | NO <sub>x</sub> removal (%) | Startup date |
|------------|------------------|-----------|-----------------------------------|-----------------------------|--------------|
| Sorami     | Boiler           | Kerosene  | 3,490                             | 62                          | Oct. 1976    |
| "          | SNS <sup>a</sup> | Naphtha   | 2,570                             | 56                          | "            |
| "          | NE <sup>b</sup>  | "         | 3,540                             | 67                          | "            |
| "          | Boiler           | Kerosene  | 3,840                             | 54                          | Oct. 1977    |
| "          | SNS              | Naphtha   | 4,362                             | 44                          | "            |
| "          | NE               | "         | 6,216                             | 58                          | "            |
| "          | Boiler           | Kerosene  | 3,870                             | 54                          | Nov. 1977    |
| "          | SNS              | Naphtha   | 4,762                             | 44                          | "            |
| "          | NE               | "         | 6,216                             | 58                          | "            |
| "          | SNS              | "         | 3,168                             | 44                          | Dec. 1977    |
| "          | NE               | "         | 4,166                             | 58                          | "            |
| "          | Boiler           | "         | 3,169                             | 44                          | June 1978    |
| "          | NE               | "         | 4,166                             | 58                          | "            |
| "          | Boiler           | Low-S oil | 10,700                            | 60                          | July 1978    |
| "          | SNS              | "         | 3,800                             | 62                          | "            |
| "          | NE               | "         | 5,200                             | 62                          | "            |
| Chita      | NH <sup>c</sup>  | Kerosene  | 6,000                             | 50                          | Oct. 1977    |
| "          | SNS              | "         | 4,300                             | 50                          | "            |
| "          | NH               | "         | 3,200                             | 50                          | "            |

<sup>a</sup>Steam naphtha superheater<sup>b</sup>Naphtha evaporator<sup>c</sup>Naphtha heater

temperature range----900-1,030°C without H<sub>2</sub> and 700-900° with H<sub>2</sub>. Hydrogen may be used at refineries and petrochemical plants but is not appropriate for use at power plants.

SNR also may be suitable for certain types of furnaces that have relatively long gas retention times at the appropriate temperatures. Over 60% NO<sub>x</sub> reduction may be attained with these furnaces. On the other hand, a removal efficiency of 30-40 percent may be a practical limit for utility boilers which must maintain unreacted NH<sub>3</sub> at a low level even during load fluctuations.

SNR works well in an emergency situation when 40-50 percent removal of NO<sub>x</sub> is needed temporarily. In this application, however, the maintenance of the ammonia injection nozzles may present a problem, since they must be kept cool at all times. MHI's cooling system which uses boiler water can be used to reduce the cooling costs.

SNR also may be useful for treating very dirty gas such as gas from a glass melting furnace or a municipal incinerator which contains particulates and gases capable of poisoning SCR catalysts.

A combined SNR/SCR system can be used to attain a higher NO<sub>x</sub> removal efficiency (50-70 percent) than can be attained by SNR alone. This combination is described in the following section.

### 6.3 SNR/SCR COMBINED SYSTEMS

#### 6.3.1 Introduction

Between 1978 and 1980, both Toyko Electric and Kamsai Electric conducted large-scale tests of combined SNR/SCR systems applied to existing oil-fired boilers. In the combined system, 1000°C ammonia is injected into the boiler for SNR; the 300-400°C gas leaving the boiler economizer is sent through a small amount of parallel-flow SCR catalyst (located in the existing duct) for further reduction of NO<sub>x</sub> and NH<sub>3</sub>. The combined system's advantage is that

it removes 50-60 percent of  $\text{NO}_x$  in flue gas from an existing boiler, requires neither an SCR reactor nor an additional fan, and produces less than 10 ppm of unreacted  $\text{NH}_3$ .

#### 6.3.2 Tokyo Electric's SNR/SCR Demonstration Plants

Tokyo Electric's three SNR/SCR demonstration plants are described in Table 6-11. All of the combined units were installed for existing oil-fired boilers which burn low-sulfur oil and produce a flue gas with 120-200 ppm  $\text{NO}_x$ .

The SNR/SCR system for the No. 2 oil-fired boiler (350 MW) at Tokyo Electric's Ohi Power Station is shown in Figure 6-10. Fifty ammonia injection nozzles, each with 40 holes, were installed at one location in the boiler where the gas temperature is about  $1,000^\circ\text{C}$  at full load. A honeycomb catalyst, ( $87 \text{ m}^3$  ( $\text{SV } 11,720 \text{ hr}^{-1}$ )), was installed in the duct between the economizer and the air preheater. For test purposes, honeycomb catalysts with different compositions and channel diameters, ranging from 8 to 10 mm, were used. The pressure drop through the catalysts bed was less than 30 mm  $\text{H}_2\text{O}$ .

The combined system at Tokyo Electric's Yokosuka Station is shown in Figure 6-11. It has ammonia injection nozzles at two locations in order to compensate for changes in the gas temperature.

The demonstration plants operated for 7,900 - 10,700 hours as shown in Table 6-11. Similar results concerning  $\text{NO}_x$  removal efficiency and unreacted  $\text{NH}_3$  were obtained at all three plants. A typical example of a test result is shown in Figures 6-12 and 6-13. By using 2.0-2.5 mol  $\text{NH}_3$  to 1 mol  $\text{NO}_x$ , the  $\text{NO}_x$  removal efficiency was 50-60 percent with unreacted  $\text{NH}_3$  below 10 ppm. Roughly 20 percent of the  $\text{NO}_x$  was removed by SNR; the rest was removed by SCR.

The  $\text{NO}_x$  removal efficiency was higher at the smaller boiler load as shown in the Figure 6-13. The reduced load was unfavorable for SNR because of the decrease in the gas temperature but increased the SCR efficiency because

TABLE 6-11. TOKYO ELECTRIC'S SNR/SCR DEMONSTRATION PLANTS (5)

| Power Station<br>and Unit No.                                      | Yokosuka No.4                     | Ohi No.2                                   | Yokohama No.1            |
|--------------------------------------------------------------------|-----------------------------------|--------------------------------------------|--------------------------|
| Capacity in MW<br>(m <sup>3</sup> N/H)                             | 350<br>(1,076,000)                | 350<br>(1,020,000)                         | 175<br>(531,000)         |
| Fuel                                                               | Low sulfur oil                    | Low sulfur oil                             | Low sulfur oil           |
| Sulfur content in<br>fuel (wt %)                                   | 0.1 ~ 0.2                         | 0.1                                        | 0.1 ~ 0.2                |
| Dust in flue gas, mg/Nm <sup>3</sup><br>(at economizer outlet)     | Approximately 50                  |                                            |                          |
| NO <sub>x</sub> in flue gas, ppm                                   | 200 ~ 120                         |                                            |                          |
| NO <sub>x</sub> reduction efficiency                               | More than 50 percent              |                                            |                          |
| Residual ammonia                                                   | Less than 10 ppm                  |                                            |                          |
| Ammonia injection<br>(NH <sub>3</sub> /NO <sub>x</sub> mole ratio) | 1.5 ~ 2.5                         |                                            |                          |
| Type of catalyst                                                   | Honeycomb<br>& plate              | Honeycomb                                  | Plate                    |
| Test Period                                                        | Apr. 1978<br>~ Aug. 1980          | June 1978<br>~ Sep. 1980                   | Aug. 1978<br>~ Sep. 1980 |
| Operating Hours                                                    | 7,900                             | 10,700                                     | 10,500                   |
| Manufacturer                                                       | Mitsubishi<br>Heavy<br>Industries | Ishikawajima<br>Harima Heavy<br>Industries | Babcock<br>Hitachi       |

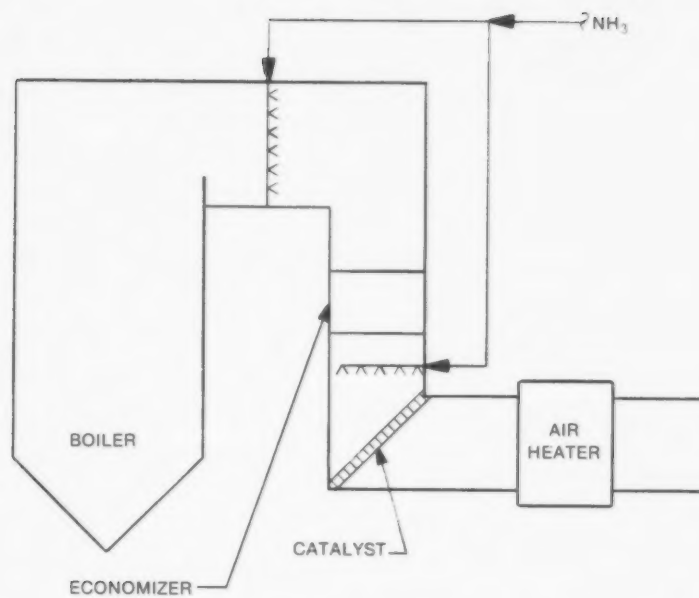


Figure 6-10 Simplified Flowsheet of the Combined SNR/SCR System at Tokyo Electric's Ohi Station.



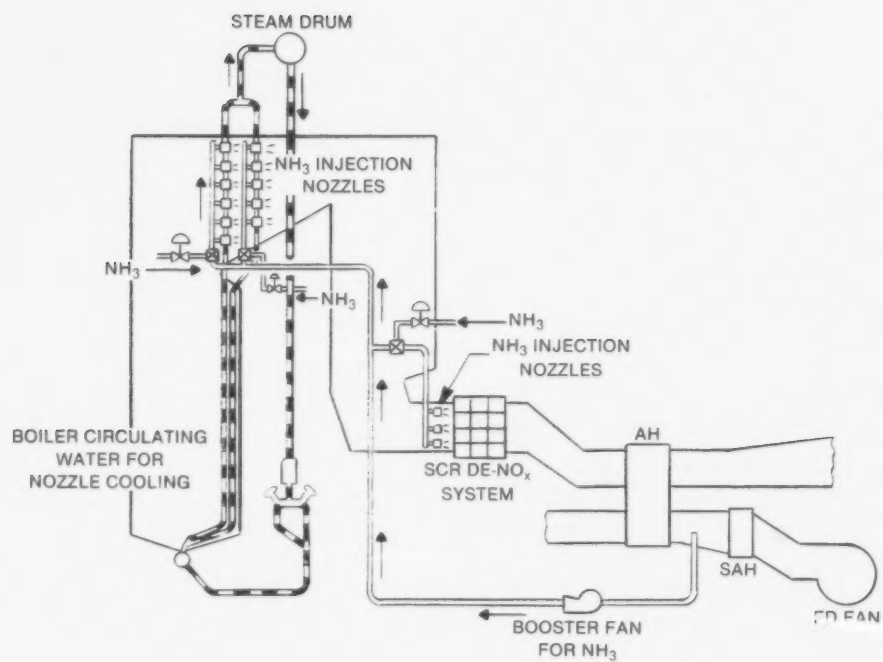


Figure 6-11 Schematic Diagram of the Combined SNR/SCR System at Tokyo Electric's Yokosuka Station. (2)

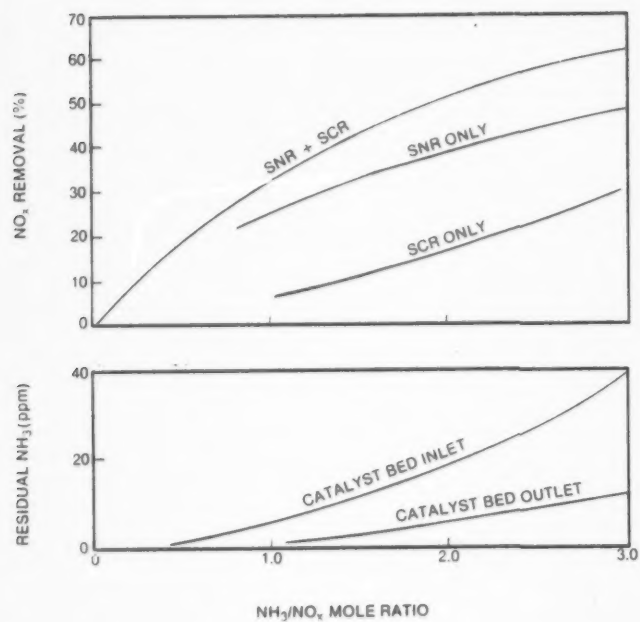


Figure 6-12 Typical Operation Data for Tokyo Electric's Combined SNR/SCR System. (2)

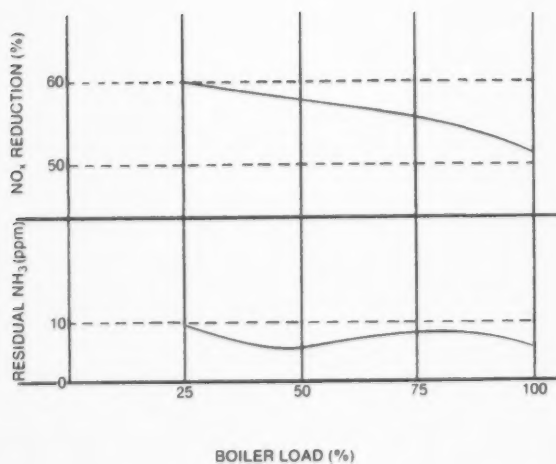


Figure 6-13 Tokyo Electric's Test Data: Effect of Boiler Load on the SNR/SCR Combined System. (5)

of the smaller SV (longer reaction time through the catalyst bed). The increased SCR efficiency was more than sufficient to compensate for the decrease in SNR efficiency.

The catalyst was effective not only for increasing  $\text{NO}_x$  removal efficiency but also for reducing unreacted  $\text{NH}_3$  below 10 ppm. Unfortunately, the air preheaters experienced ammonium bisulfate plugging. The only exception was at the Ohi plant which only had a slight bisulfate problem probably because of the low sulfur content of its fuel. The air preheaters at the other stations required water washing once every 3 or 4 months.

The demonstration tests were completed in September 1980. At that time the SNR ammonia injection nozzles were removed. Since that time, at the Ohi plant a small amount of ammonia ( $0.15 - 0.2 \text{ mol NH}_3/\text{mol NO}_x$ ) has been injected through the nozzles for SCR to remove 15-20% of  $\text{NO}_x$  with 2-3 ppm of unreacted  $\text{NH}_3$ .

Use of the SNR systems was discontinued for several reasons. First, the local  $\text{NO}_x$  regulation can be met using combustion modification. For example, the  $\text{NO}_x$  regulation for the Ohi No. 2 boiler is 140 ppm. This level can be achieved by using combustion modification, including staged combustion, flue gas recirculation and a low- $\text{NO}_x$  burner. For safety reasons, 15-20% of  $\text{NO}_x$  from the boiler is removed by SCR. Second, because of the high temperatures in which they were used, the SNR ammonia injection nozzles caused maintenance problems. Another reason was that in the SNR system the ammonia consumption is high and the unreacted  $\text{NH}_3$  is higher than it would be in a standard SCR plant. This caused ammonium bisulfate deposition problems in two plants.

#### 6.3.3 Kansai Electric's Full-Scale SNR Test

In October 1977, Kansai Electric installed a full-scale SNR test unit for an existing 156 MW oil-fired boiler at the Himeji No. 1 Station. In July 1978, a small amount of SCR catalyst was placed in the duct between the boiler economizer and air preheater to increase  $\text{NO}_x$  removal efficiency to 50-70% and to reduce unreacted  $\text{NH}_3$ .

In 1979, the SNR unit was removed primarily because of the maintenance problems associated with the ammonia injection nozzles. Since that time, the SCR catalyst successfully has removed about 30% of the  $\text{NO}_x$  with little catalytic degradation.

#### 6.3.4 Evaluation

A combined SNR/SCR system was once considered ideal for removal of 50-60% of  $\text{NO}_x$  in flue gas from existing boilers. However, maintenance of the system's ammonia injection nozzles proved to be a serious drawback. For most existing utility boilers, a standard SCR reactor can be retrofitted between the boiler economizer and the air preheater to remove over 80% of  $\text{NO}_x$ . Alternatively, a parallel flow catalyst placed in the existing duct can remove 30-40% of  $\text{NO}_x$ .

The combination system still may be valuable for removing 50-60% of  $\text{NO}_x$  from existing furnaces and boilers that have no space for installation of SCR reactors.

### 6.4 MITSUBISHI ADVANCED COMBUSTION TECHNOLOGY (MACT) IN-FURNACE $\text{NO}_x$ REMOVAL PROCESS

#### 6.4.1 Introduction

MHI developed the Mitsubishi Advanced Combustion Technology (MACT) in-furnace process to remove about 50% of  $\text{NO}_x$  from a boiler. In the process the secondary fuel--about 10% of the fuel for the boiler--is used as a reducing agent. At temperatures above 1200°C the secondary fuel is injected into the boiler combustion gas to create a reducing atmosphere. In this atmosphere 70-90% of  $\text{NO}_x$  is converted to  $\text{N}_2$  and  $\text{H}_2\text{O}$  and additional air is injected for complete combustion (Figure 6-14). Since a small amount of  $\text{NO}_x$  is formed during the complete combustion stage, the overall  $\text{NO}_x$  removal efficiency of the process is usually about 50%.

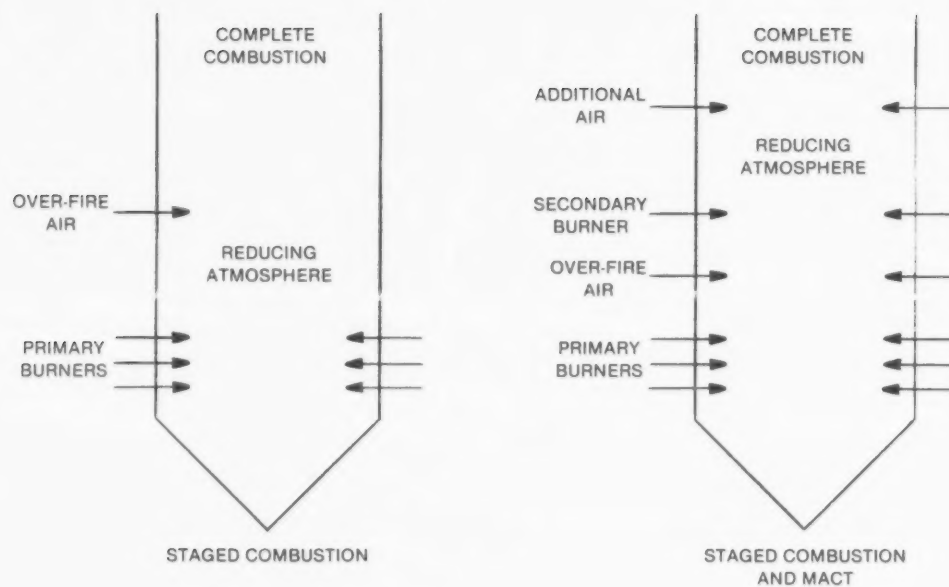


Figure 6-14 Staged Combustion and Staged Combustion/MACT Processes.

After completing small-scale tests, MHI joined with Tokyo Electric to conduct pilot plant tests using corner-firing furnaces. With a combination of combustion modification and MACT, NO<sub>x</sub> concentrations were lowered to about 60 ppm for coal, 30 ppm for oil and 10 ppm for gas fuels. Tokyo Electric has been using the MACT/staged combustion system commercially for two small oil-fired boilers (125 MW each) which were originally designed to burn coal. The system has reduced NO<sub>x</sub> to 30-40 ppm.

#### 6.4.2 Small-Scale Tests (6,7)

Figure 6-15 and Table 6-12 provide a description of the small MACT test furnace. The compositions of the domestic low-sulfur coals which were used for the test are shown in Table 6-13.

TABLE 6-12. SMALL TEST FURNACE SPECIFICATIONS

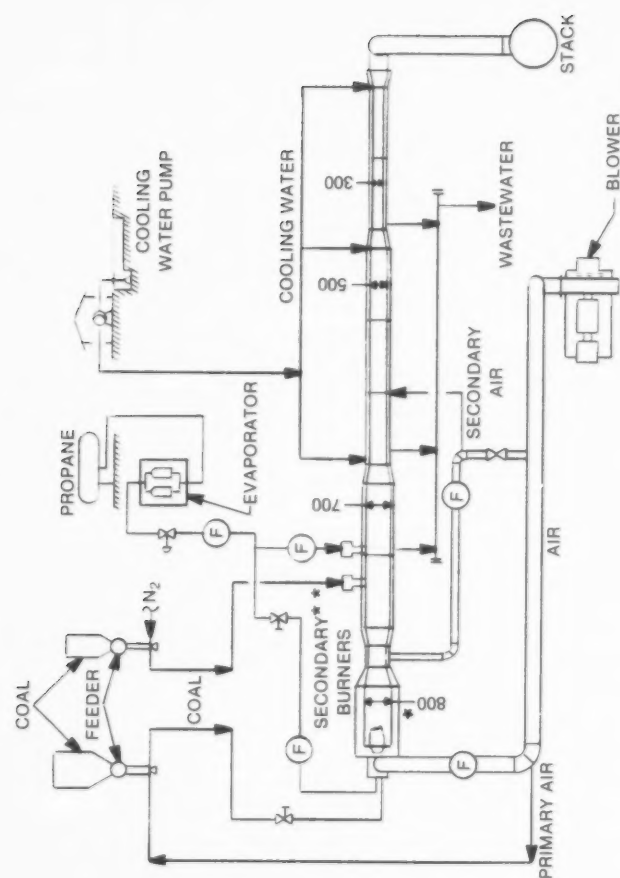
|                  |                                                                                                                                       |
|------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| Furnace          | Diameter 0.8 m<br>Length 2.2 m<br>Castable refractory-lined cylindrical furnace                                                       |
| Primary burner   | Propane (10 kg/hr) or pulverized coal (100 kg/hr)<br>Air at room temperature                                                          |
| Secondary burner | Propane or pulverized coal 10 kg/hr<br>Air at room temperature is used for combustion.<br>Pulverized coal is carried by nitrogen gas. |

TABLE 6-13. COMPOSITION AND HEAT VALUE OF COALS (200 mesh 90% pass)

|                   | Ash<br>(%) | Volatile<br>(%) | Fixed<br>Carbon<br>(%) | Moisture<br>(%) | N<br>(%) | S<br>(%) | Heat Value<br>(kcal/kg) |
|-------------------|------------|-----------------|------------------------|-----------------|----------|----------|-------------------------|
| Small scale tests | 13.2       | 42.2            | 38.4                   | 6.2             | 1.0      | 0.28     | 6220                    |
| Pilot plant tests | 10.1       | 42.6            | 40.8                   | 6.5             | 1.0      | 0.20     | 6400                    |

Figure 6-16 illustrates test results when propane fuel was used. Propane was burned in the primary burner producing a flue gas containing 140 ppm NO and 1% O<sub>2</sub>. A reducing gas formed by the partial combustion of the propane (10% of primary fuel) was introduced into the flue gas at 1,200°C; this





(F) : FLOW METER

\* Dimensions are in mm.

\*\* Location of the secondary burner is changeable.

Figure 6-15 Flowsheet of a Small-Scale MACT Test Plant.

reduced NO to 25 ppm. For complete combustion, additional air was introduced. This had the effect of increasing NO to 70 ppm, resulting in an overall NO<sub>x</sub> removal efficiency of 50%.

Figure 6-17 shows that NO<sub>x</sub> was reduced when the secondary fuel was injected above 750°C and that the NO<sub>x</sub> removal efficiency was higher when the flue gas contained a lower O<sub>2</sub> concentration before the secondary fuel injection.

Figure 6-18 shows the results of a test using a low-NO<sub>x</sub> burner with pulverized coal fuel. The NO concentration ranged from 100 to 150 ppm before the secondary fuel was injected, and was reduced to 50 to 60 ppm by the MACT. The gas at the stack contained 10 ppm CO, but no hazardous gases such as HCN.

#### 6.4.3 Fundamental MACT Studies (6)

Figures 6-19 and 6-20 show the NO<sub>x</sub> decomposition ratio that occurred with propane fuel before the introduction of the additional air for complete combustion. The decomposition ratio was influenced by  $\lambda$ , which is defined by the following equation:

$$\lambda = \frac{\text{Inlet O}_2 \text{ (O}_2 \text{ in flue gas before secondary fuel was added)}}{\text{O}_2 \text{ required for complete combustion of the secondary fuel}}$$

About 90% of NO was decomposed at 1,150 - 1,300°C when  $\lambda$  was 0.18 and 0.53, while the decomposition ratio was only about 10% when  $\lambda$  was 2.2. At 1,300°C a reaction time of 0.1 second was sufficient for decomposition when  $\lambda$  was 0.53. Figure 6-20 shows that the decomposition ratio was not influenced by the inlet NO concentration, which ranged from 30 to 1,000 ppm.

Figure 6-21 shows test results with different fuels. When  $\lambda$  was between 0.15 and 0.9, 80-95% of NO was decomposed for all fuels including gas, oil, and coal. The decomposition ratio was considerably lower when  $\lambda$  was below 0.1 and above 1.0. This indicates that a small amount of O<sub>2</sub> is needed for the reaction and that excessive O<sub>2</sub> prevents decomposition.

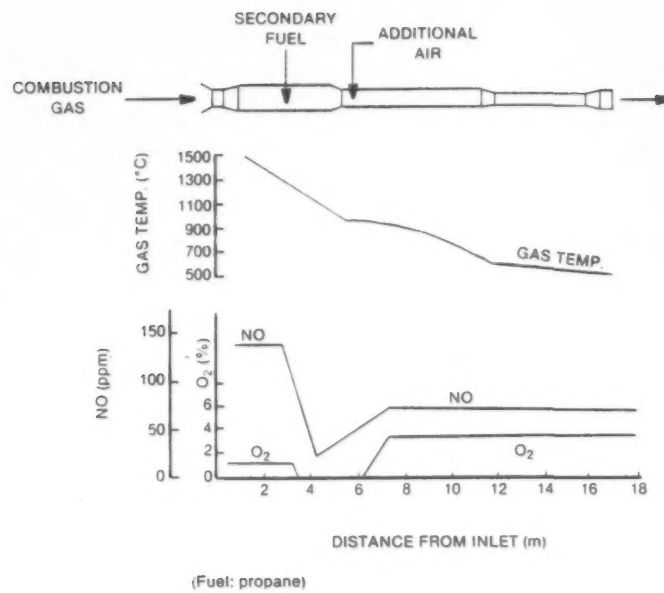


Figure 6-16 Change in NO Concentration Caused by MACT.

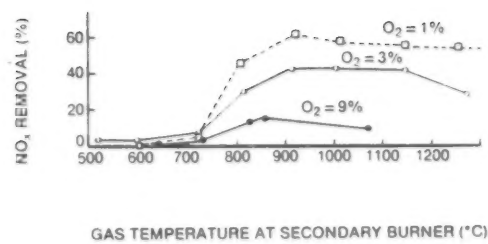
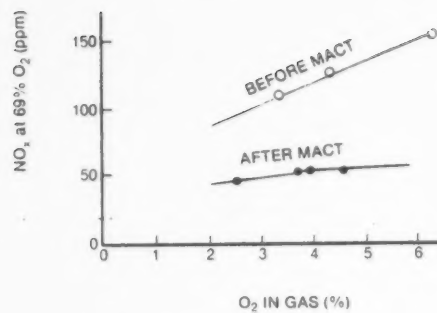
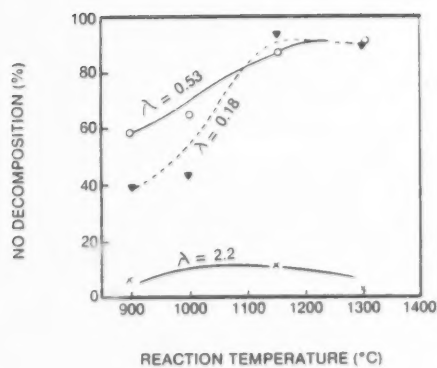


Figure 6-17 Gas Temperature, O<sub>2</sub> Percentage, and NO<sub>x</sub> Removal During MACT Treatment.



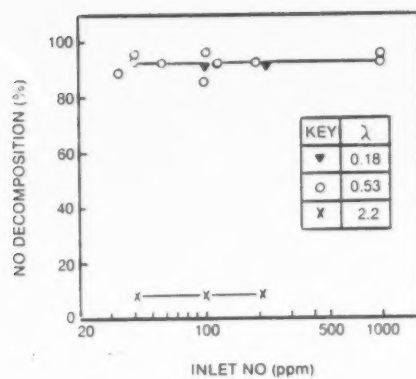
(Fuel: pulverized coal)

Figure 6-18 NO<sub>x</sub> Concentration Before and After MACT Treatment.



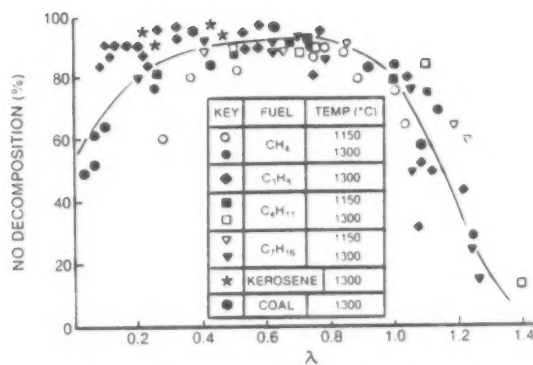
(Inlet O<sub>2</sub>: 1%; inlet NO: 92-103 ppm; reaction time: 0.2 sec;  
gas volume: 5 NI/min; fuel: propane)

Figure 6-19 NO Decomposition Ratio at Different Temperatures and O<sub>2</sub> Concentrations.



(Fuel: propane, 1300°C; reaction time: 0.2 sec;  
inlet O<sub>2</sub>: 1%; gas volume: 5 NI/min)

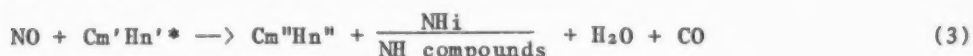
Figure 6-20 Inlet NO and Decomposition Ratio.



(1300°C, 0.2 sec; O<sub>2</sub>: 0.1-10%; inlet NO: about 80 ppm;  
gas volume: 5 NI/min)

Figure 6-21 Relationship Between  $\lambda$  and NO Decomposition for Various Fuels.

The decomposition reactions are assumed to be these:



\*indicates radical

Hydrocarbon (secondary fuel) is decomposed by  $\text{O}_2$  to form hydrocarbon radical (1), which reacts with NO to form  $\text{N}_2$  (2) and  $\text{NH}_i$  or nitrogen hydrogen compounds such as  $\text{NH}_3$  and  $\text{NH}_2$  (3).

Figure 6-22 shows the relationship between the amount of NO decomposed and the amount of  $\text{NH}_i$  formed from the NO. When less than 40 ppm NO was decomposed, nearly all of the NO was converted to  $\text{NH}_i$ ; the conversion ratio decreased as the amount of decomposed NO increased. This indicates that the MACT process may work more efficiently with flue gas richer in NO.

The reactions which take place during complete combustion by air addition are shown below:



The nitrogen hydrides,  $\text{NH}_2$  and  $\text{NH}_3$ , shown as  $\text{NH}_i$ , may be converted to both  $\text{N}_2$  and NO. The conversion of  $\text{NH}_i$  to NO occurs at temperatures above  $700^\circ\text{C}$  as shown in Figure 6-23; the conversion ratio is higher with a higher  $\text{O}_2$  concentration in the gas.



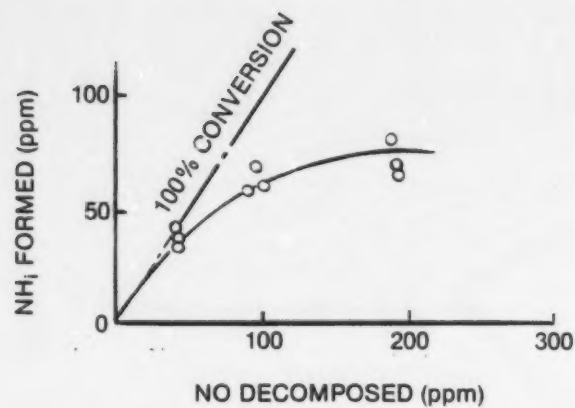


**Figure 6-22** Conversion of NO to NHI by Secondary Fuel Addition.

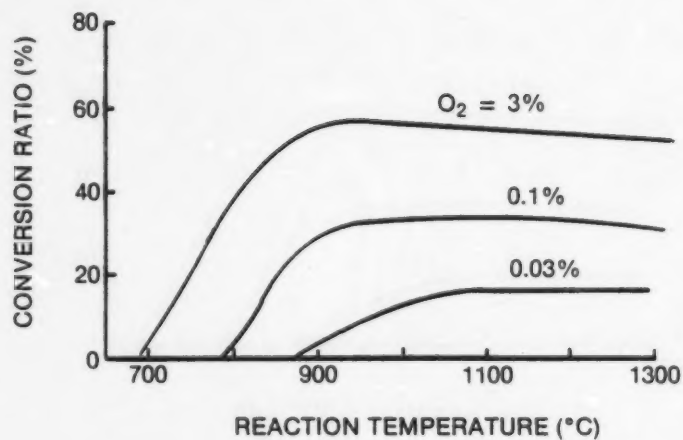


**Figure 6-23** Conversion of NHI to NO<sub>x</sub> by Air Addition for Complete Combustion.

#### 6.4.4 Pilot Plant Tests with Corner-firing Furnaces(7)

As shown in Table 6-14, pilot plant tests of MACT were conducted with two corner-firing furnaces. The operating conditions and the coals used for the pilot plant tests are shown in Tables 6-15 and 6-13, respectively.

TABLE 6-14. FURNACE SPECIFICATIONS

| Fuel                                                                | Gas and Oil        | Coal                |
|---------------------------------------------------------------------|--------------------|---------------------|
| Heat capacity (10 <sup>7</sup> Kcal/hr)                             | 1.5                | 2.0                 |
| Number of burners                                                   | 12 (gas), 8 (oil)  | 12                  |
| Forced draft fan (m <sup>3</sup> /min)<br>(mmH <sub>2</sub> O)      | 450 (20°C)<br>800  | 920 (20°C)<br>800   |
| Induced fan (m <sup>3</sup> /min)<br>(mmH <sub>2</sub> O)           | 650 (300°C)<br>200 | 1140 (100°C)<br>800 |
| Gas recirculation fan (m <sup>3</sup> /min)<br>(mmH <sub>2</sub> O) | 427 (500°C)<br>400 | 760 (350°C)<br>600  |
| Air preheater (Nm <sup>3</sup> /min)                                | 430 (288°C)        | 750 (350°C)         |

TABLE 6-15. MACT PILOT PLANT TEST CONDITIONS

| Fuel                                 | Gas     | Oil     | Coal     |
|--------------------------------------|---------|---------|----------|
| Main burner                          |         |         |          |
| Type                                 | PM      | PM      | SGR      |
| Fuel (kg/hr)                         | 240-800 | 200-800 | 600-1200 |
| Gas recirculation (%)                | 0-30    | 0-20    | 0-10     |
| Over fire air (%)                    | 0-20    | 0-20    | 0-20     |
| Secondary burner                     |         |         |          |
| Fuel (kg/hr)                         | 0-150   | 0-150   | 0-150    |
| Gas recirculation (%)                | 0-15    | 0-15    | 5-15     |
| Additional air (%)                   | 0-20    | 0-20    | 0-20     |
| O <sub>2</sub> at furnace outlet (%) | 1-3     | 1-3     | 2-4      |

The furnace was operated manually. As shown in Figure 6-24, furnace operation stabilized three to five minutes after the use of MACT began.

Figures 6-25 to 6-27 show the relationship between  $O_2$  concentrations in the flue gas (prior to the injection of the secondary fuel) and  $NO_x$  concentrations with and without MACT. Using a combination of combustion modification and MACT, NO was reduced to 7-10 ppm for gas, 40-50 ppm for oil, and 50-70 ppm for coal. Figure 6-28 shows the effect of MACT for oil-burning when the nitrogen content of the oil was increased to 0.9% by adding pyridine. NO was maintained at 70 ppm even for oil containing 0.9% N.

An analysis of both the flue gas and the fly ash leaving the MACT system indicated that MACT did not cause any degradation in their composition and properties.

#### 6.4.5 Evaluation

The MACT in-furnace process requires the same investment and operation expenditures as the process of combustion modification by staged combustion. By combining combustion modification and MACT,  $NO_x$  in flue gas from a large utility boiler may be reduced to about 100 ppm for coal, 40 ppm for oil, and 20 ppm for gas. Process operation appears to be problem-free.

A disadvantage associated with MACT is that it requires a furnace that is about 10% taller than most conventional furnaces. For this reason, MACT may not be applied to most existing boilers without a reduction in boiler capacity. An exception to this is the type of the boiler used commercially by Tokyo Electric. This boiler was originally designed for burning coal and oil and has a very large furnace for oil-firing.

The MACT process may be useful for a new boiler, especially for a coal-fired boiler in which  $NO_x$  reduction to 100 ppm is needed. For 50%  $NO_x$  reduction, the MACT may be more advantageous than selective noncatalytic

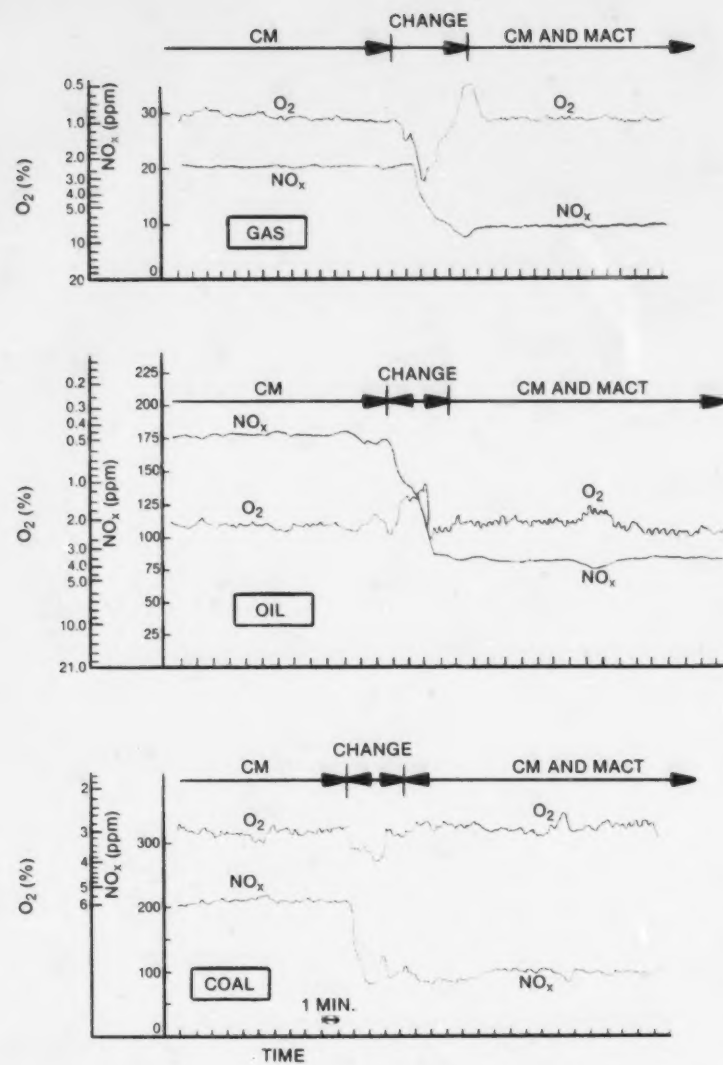


Figure 6-24  $O_2$  Percentage and  $NO_x$  Concentration After Combustion Modification (CM) and CM Plus MACT in a Corner-Firing Furnace Using Three Fuels.

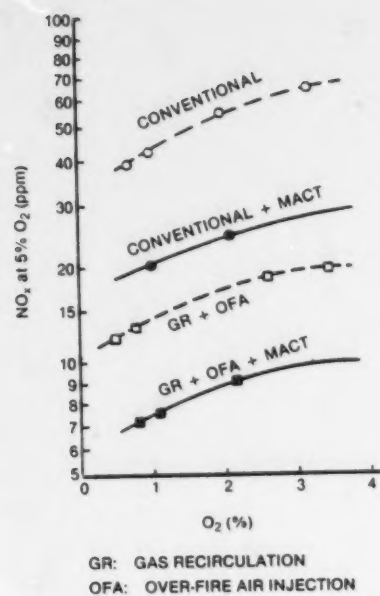


Figure 6-25 Results of MACT Pilot Plant Tests with Propane Fuel. (624 kg/hr)

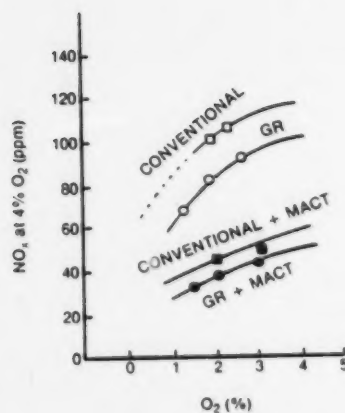


Figure 6-26 Results of MACT Pilot Plant Test with Heavy B Oil Fuel. (N: 0.12%, 800 l/hr)

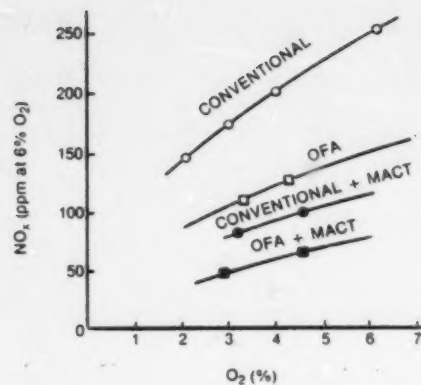
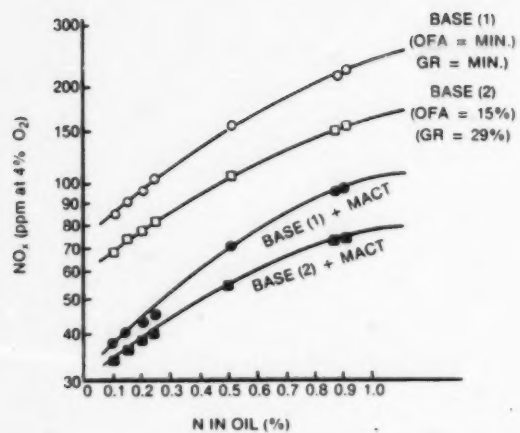


Figure 6-27 Results of MACT Pilot Plant Tests with Coal Fuel. (1150 kg/hr)



\* O<sub>2</sub> was 2% before the addition of the secondary fuel.

Figure 6-28 Results of MACT Pilot Plant Tests with Oil Containing Pyridine\*.



reduction (Thermal DeNO<sub>x</sub>) because MACT does not require ammonia and therefore does not have an ammonium bisulfate problem. For additional NO<sub>x</sub> abatement, selective catalytic reduction (SCR) must be used with MACT.

IHI, Babcock Hitachi (BH), and Tokyo Electric have tested a process similar to MACT and have obtained about 50% NO<sub>x</sub> removal. In addition, Hitachi Zosen has developed a similar process for industrial boilers (Section 6.9.5) (8). The MACT process may be best suited to corner-firing (tangential firing) boilers. It is based on rapid uniform mixing of the secondary fuel with combustion gas which can be attained easily in that type of boiler.

## 6.5 ACTIVATED CARBON PROCESS (EPDC - SHI PROCESS)

### 6.5.1 Introduction

EPDC and Sumitomo Heavy Industries (SHI) have conducted tests of the activated carbon process with the objective of removing 95% of SO<sub>x</sub> and 40% of NO<sub>x</sub> in flue gas from a coal-fired boiler. They have operated a pilot plant with a capacity of treating 10,000 Nm<sup>3</sup>/hr of flue gas from a coal-fired boiler at EPDC's Takehara Station since November 1978.

In the activated carbon process, the SO<sub>2</sub> adsorbed by the carbon is regenerated by heating and converted to elemental sulfur by the RECLAUS process. In the RECLAUS process, SO<sub>2</sub> is reduced to H<sub>2</sub>S and S using coal, and then the H<sub>2</sub>S and the SO<sub>2</sub> react in the Claus furnace to form byproduct elemental sulfur. Ammonia is added to the flue gas to: 1) increase SO<sub>x</sub> removal efficiency, 2) reduce carbon consumption by thermal regeneration, and 3) remove a portion of the NO<sub>x</sub>.

An activated carbon process demonstration plant sponsored by the Ministry of International Trade and Industry will be completed in 1983. The plant will be located at EPDC's Matsushima Station and will have a capacity of treating 300,000 Nm<sup>3</sup>/hr of flue gas from a coal-fired boiler.

### 6.5.2 Pilot Plant Test of the Activated Carbon Process (9)

The composition of the flue gas and the pilot plant test conditions at EPDC's Takehara Station are shown in Tables 6-16 and 6-17.

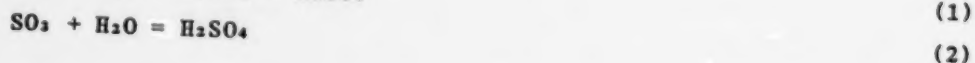
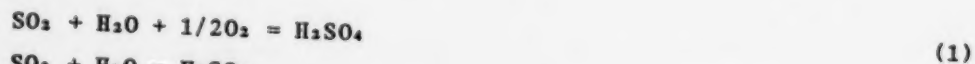
TABLE 6-16. FLUE GAS COMPOSITION DURING PILOT PLANT TEST

|                          | Range    | Average |
|--------------------------|----------|---------|
| SO <sub>2</sub> , ppm    | 600-1000 | 900     |
| NO <sub>x</sub> , ppm    | 200-400  | 250     |
| O <sub>2</sub> , %       | 5.0-8.9  | 6.6     |
| CO <sub>2</sub> , %      | 12.0     | 12.0    |
| H <sub>2</sub> O, %      | 8.1-9.0  | 8.4     |
| Dust, mg/Nm <sup>3</sup> | 140-310  | 250     |

TABLE 6-17. TEST CONDITIONS

|                                       |          |
|---------------------------------------|----------|
| SO <sub>2</sub> , ppm                 | 600-1000 |
| NO, ppm                               | 200-350  |
| Gas temperature, °C                   | 120-150  |
| Space velocity (SV), hr <sup>-1</sup> | 500-900  |

A flowsheet of the pilot plant is presented in Figure 6-29. Ammonia is added to the flue gas in the ratio of 0.5 mol ammonia/mol SO<sub>x</sub> and the gas is sent horizontally through a moving bed in which granular activated carbon moves downward. The SO<sub>x</sub> in the gas is adsorbed by the carbon to form sulfuric acid:



A portion of the ammonia reacts with the sulfuric acid to form ammonium bisulfate while the rest of it is reacted with NO by the catalytic action of the carbon:

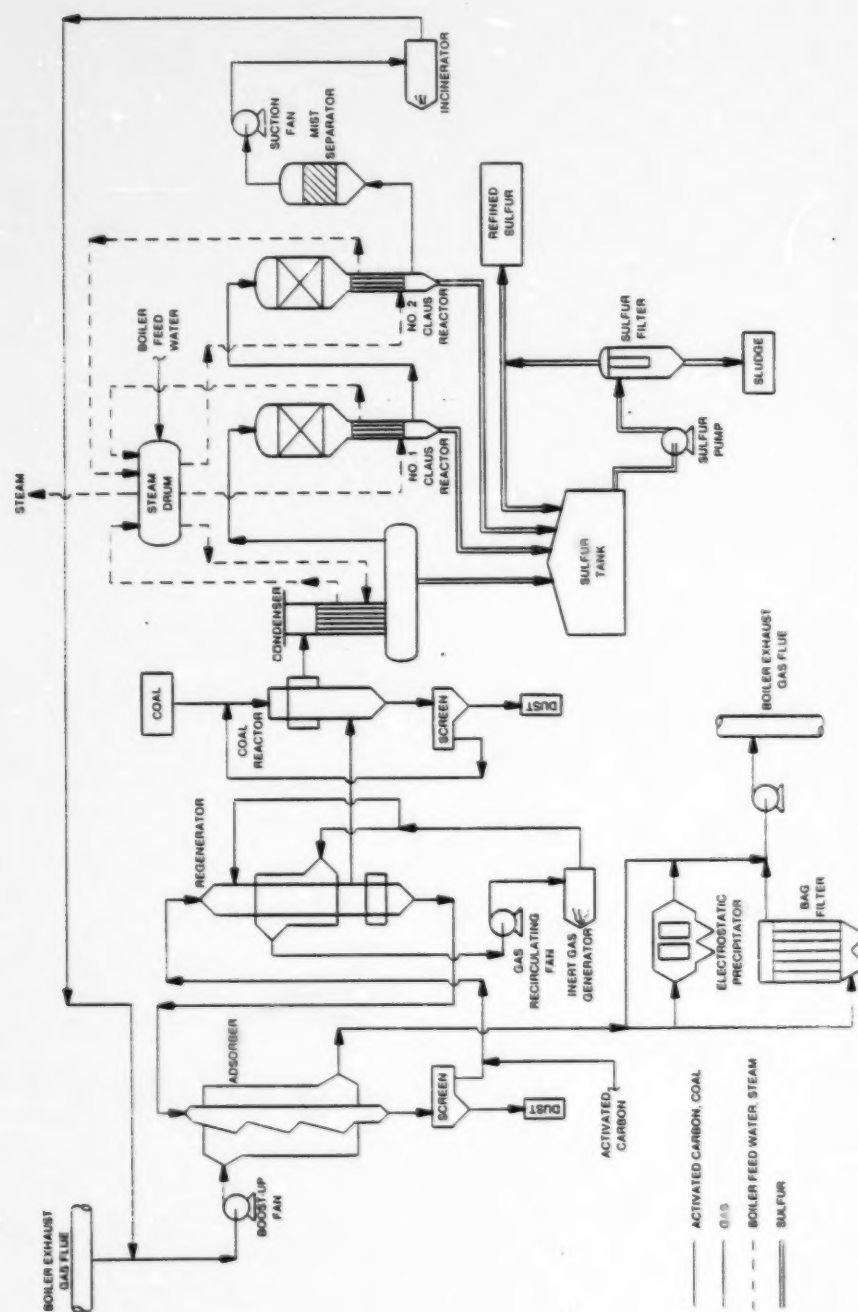
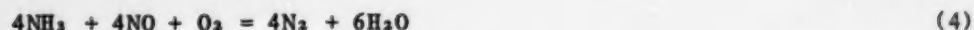
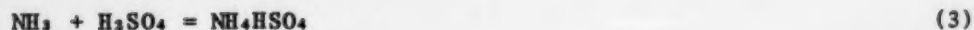
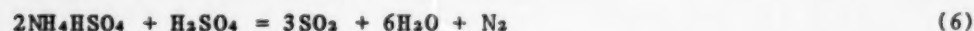


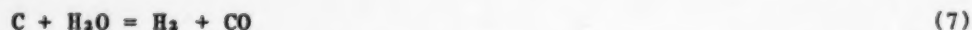
Figure 6-29 Flowsheet for the Activated Carbon Process Pilot Plant at EPDC's Takehana Station. (9)



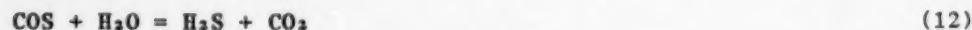
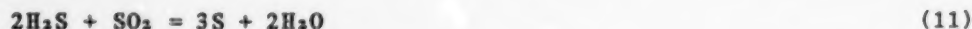
The relationship of reaction temperature to removal efficiency in the system is shown in Figure 6-30. The flue gas is then sent through an ESP or a baghouse and on to the stack. Loaded with ammonium bisulfate and sulfuric acid, the carbon is discharged from the bed and sent into another moving bed reactor (regenerator). There it is heated above 350°C by an inert gas produced by the incomplete combustion of fuel. The treated carbon is returned to the adsorber and the  $\text{SO}_2$  is regenerated by the following reactions:



The  $\text{SO}_2$ -rich gas leaving the regenerator is mixed with a small amount of air and sent to the bottom of the coal reactor, a shaft furnace charged with coal. As a result of the partial combustion of the coal, the gas temperature in the reactor reaches about 900°C. This causes the following reactions:



About 80% of the  $\text{SO}_2$  is reacted in the furnace; about 40% forms sulfur, 30% forms  $\text{H}_2\text{S}$ , and 10% forms  $\text{COS}$ . The gas is then cooled to allow condensation of elemental sulfur, and is sent into two Claus furnaces in series. In the furnaces, nearly all of the sulfur compounds are converted to elemental sulfur:



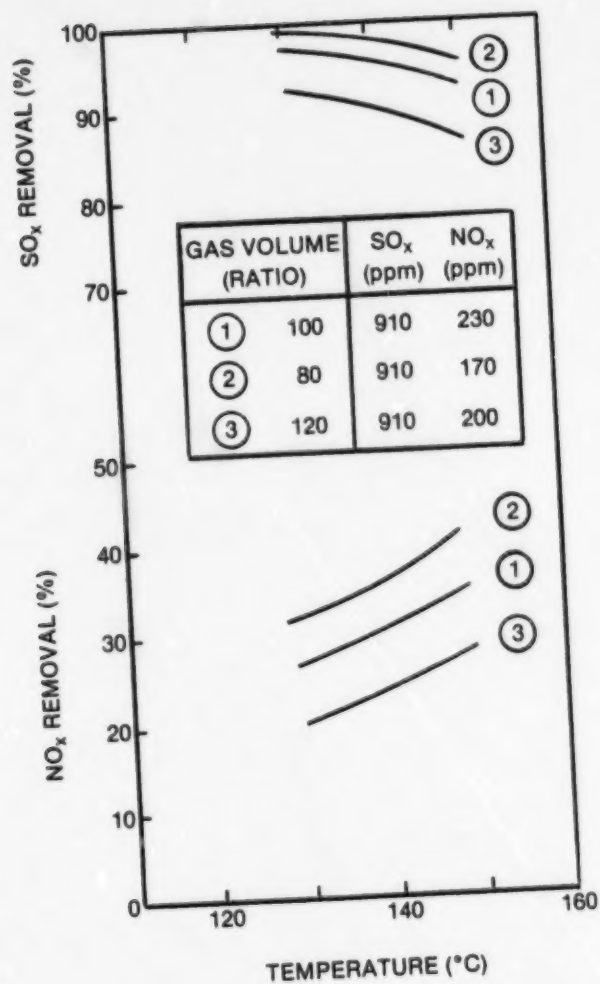


Figure 6-30 Effect of Temperature and Gas Volume on SO<sub>x</sub> and NO<sub>x</sub> Removal Efficiencies. (NH<sub>3</sub>/SO<sub>x</sub> = 0.5) (10)



In actuality, a small amount of air is added to the gas leaving the coal reactor in order to adjust the  $\text{H}_2\text{S}/\text{SO}_2$  ratio to 2. The gas leaving the Claus furnace (containing small amounts of  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and  $\text{COS}$ ) is incinerated to convert  $\text{H}_2\text{S}$  and  $\text{COS}$  to  $\text{SO}_2$  and is returned to the adsorber.

Figure 6-31 shows the  $\text{SO}_2$  and  $\text{NO}_x$  removal efficiencies during an 8,000-hour continuous test cycle at the pilot plant. The  $\text{SO}_x$  removal efficiency ranged from 80 to 99% (90-95% removal for most of the time) while the  $\text{NO}_x$  removal efficiency ranged from 20-40% (30% average). The activated carbon was consumed at a rate of 0.5-1% per day. Ammonia was not detected in the flue gas leaving the adsorber as long as the  $\text{NH}_3/\text{SO}_x$  mole ratio was kept below 0.5. The recovered sulfur contained a very small amount (less than 0.5%) of impurities such as  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_4\text{Cl}$ ; the impurities subsequently were removed by filtration to yield a byproduct sulfur with over 99.9% impurity.

### 6.5.3 Evaluation

The activated carbon process is advantageous in that it does not require either water or gas reheating, while it simultaneously removes over 90% of  $\text{SO}_x$  and about 30% of  $\text{NO}_x$ , and produces elemental sulfur. On the other hand, the process does consume a large amount of carbon even with the addition of ammonia. The cost of carbon may be one of the important factors to consider in determining the commercial applicability of the process.

The  $\text{NO}_x$  removal efficiency of the process can be increased to 80-90% by using a much larger amount of ammonia and a high quality carbon at  $230^\circ\text{C}$ . This was demonstrated by the Unitika process pilot plant. The Unitika process, however, was abandoned because of its large consumption of costly carbon and ammonia. It may be possible to use less costly carbon and smaller amounts of ammonia for about 30%  $\text{NO}_x$  removal at a lower temperature.



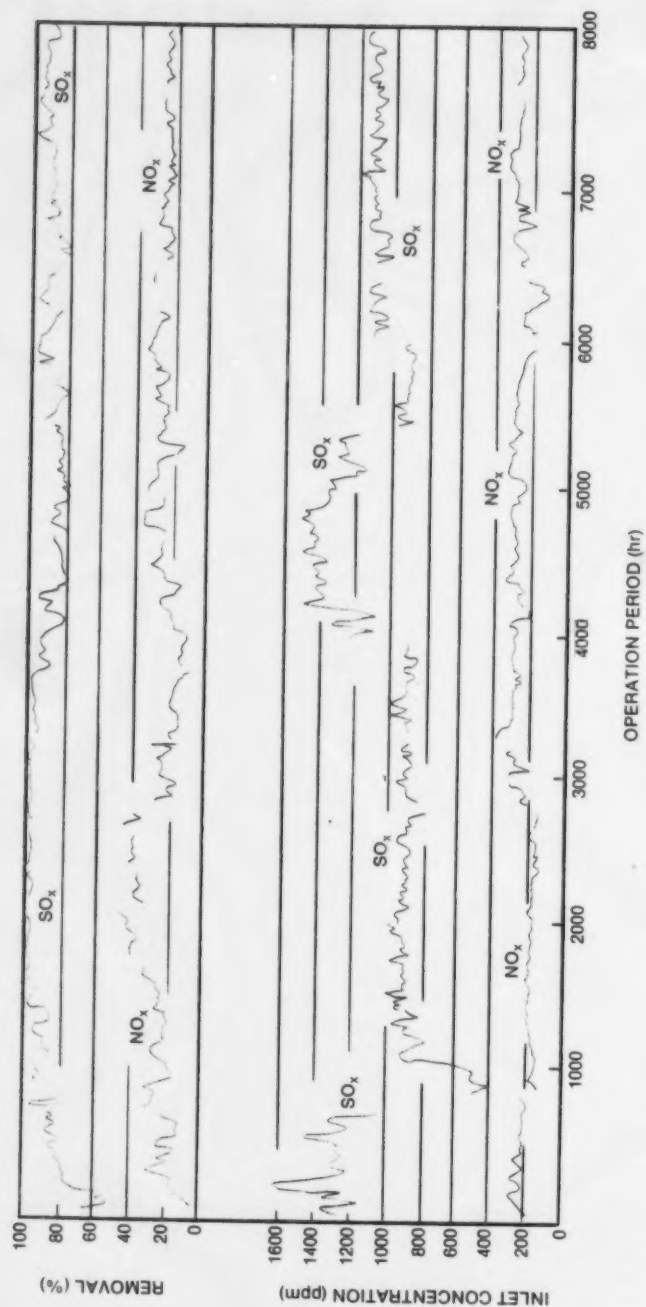


Figure 6-31 SO<sub>x</sub> and NO<sub>x</sub> Concentrations and Removal Efficiencies During an 8000 Hour Continuous Test Cycle. (9)

The activated carbon process may not be suitable for flue gas with a high  $\text{SO}_x$  content because both ammonia and carbon consumption increase with  $\text{SO}_x$  concentration; it may be well suited for flue gas from coal or oil with less than about 1% sulfur. The operation of the demonstration plant now under construction at Matsushima should provide more valuable information on the process. SHI also conducted tests on the feasibility of using 2 absorbers to remove about 80% of  $\text{NO}_x$  and 90% of  $\text{SO}_2$ . Further study is needed to evaluate this process.

## 6.6 EBARA ELECTRON BEAM IRRADIATION PROCESS

### 6.6.1 Introduction

Ebara Corporation, and the Japan Atomic Energy Research Institute, have developed a process which simultaneously removes  $\text{SO}_x$  and  $\text{NO}_x$  from flue gas by irradiating the gas with an electron beam and then collecting the resulting particulates with an ESP. From 1974-1977, Ebara operated a pilot plant with a capacity of treating 1,000  $\text{Nm}^3/\text{hr}$  of flue gas from an oil-fired boiler. Tests at this early stage of development were not very successful. Later Ebara began using ammonia, which substantially improved the process.

By irradiating the gas containing ammonia, over 90% of  $\text{SO}_x$  and 80% of  $\text{NO}_x$  can be removed, and converted to fine crystals of ammonium sulfate nitrate (double salt) which can be used for fertilizer. A larger pilot plant with a capacity of treating 3,000 to 10,000  $\text{Nm}^3/\text{hr}$  of flue gas from an iron-ore sintering machine was operated from July 1977 through June 1978 at Nippon Steel's Yawata Works. The Ebara electron beam irradiation process has been licensed to AVCO, USA.

### 6.6.2 Ebara Process Pilot Plant Tests (11, 12)

A flowsheet of the larger Ebara process pilot plant is shown in Figure 6-32. The most important pieces of equipment in the plant are: gas coolers for indirect cooling (heat exchanger) and direct cooling (water spray), an ammonia injection facility, an electron beam reactor surrounded by a concrete

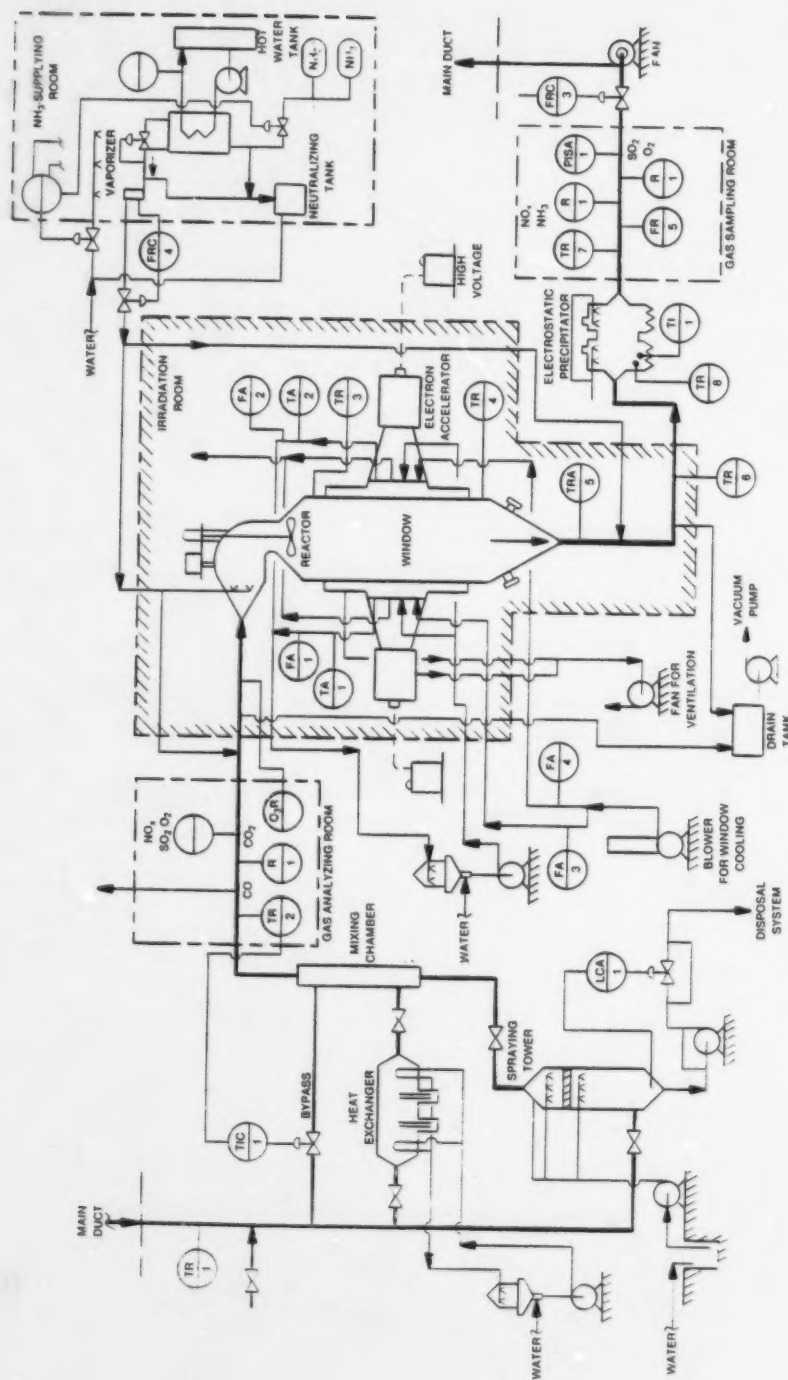


Figure 6-32 Flowsheet of an Ebara Electron Beam Process Pilot Plant.  
(3,000-10,000 Nm<sup>3</sup>/hr)

wall to prevent x-ray emissions, an ESP, and a control system. As shown in Figures 6-32 and 6-33, two electron beam accelerators with a unit capacity of 750 kV, 60 mA were placed at opposite ends of a cylindrical reactor with a diameter of 2.6 m. The distribution of the dose rate in the reactor is shown in Figure 6-33.

Since the dose rate was not uniform throughout the reactor, an impeller was placed at the reactor inlet to rotate the gas and homogenize the reaction. A side stream of the gas from an iron-ore sintering furnace was treated in the reactor. The gas contained about 200 ppm each of  $\text{SO}_2$  and  $\text{NO}_x$  (mainly NO), 40 mg/ $\text{Nm}^3$  of dust, 15.5%  $\text{O}_2$ , 10.3%  $\text{H}_2\text{O}$ , and 16.2%  $\text{CO}_2$ , and had a flow rate of 3,000–10,000  $\text{Nm}^3/\text{hr}$ . It was cooled to 70–90°C, injected with ammonia, and sent into the reactor. In some of the tests,  $\text{SO}_2$ , NO, and fly ash were added to the gas in order to simulate flue gas from coal. Ammonia was used at an average stoichiometry of 1.0 (2 mol  $\text{NH}_3$ /mol  $\text{SO}_x$  and 1 mol  $\text{NH}_3$ /mol  $\text{NO}_x$ ). For some of the tests, this stoichiometry was changed.

The relationship between the gas rotation ratio and the  $\text{NO}_x$  and  $\text{SO}_x$  removal efficiencies is shown in Figure 6-34. The gas rotation ratio is defined as:

$$\frac{\text{revolutions of impeller (rpm)}}{\text{gas flow rate (Nm}^3/\text{hr)}}$$

A maximum efficiency—over 95% for  $\text{SO}_x$  and 80% for  $\text{NO}_x$ —was obtained at the ratio of about 1/60, with 1.8 Mrad at 90°C.

The effect of the dose on removal efficiency and unreacted  $\text{NH}_3$  is shown in Figure 6-35.  $\text{SO}_x$  removal efficiency exceeded 90% at 1.3 Mrad at 70°C and at 2 Mrad at 90°C, while  $\text{NO}_x$  removal efficiency reached a maximum ---- about 80%—with 1.8 Mrad at 70°C or about 65% with 1.8 Mrad at 90°C. The decrease in  $\text{NO}_x$  removal efficiency at the higher dose level may be due to the formation of  $\text{NO}_x$  from  $\text{N}_2$  and  $\text{O}_2$ . The amount of unreacted  $\text{NH}_3$  decreased with an increasing dose and was almost zero above 1.8 Mrad at 70°C; there was a considerable amount of unreacted  $\text{NH}_3$  at 90°C even with 2.4 Mrad. The tests shown in

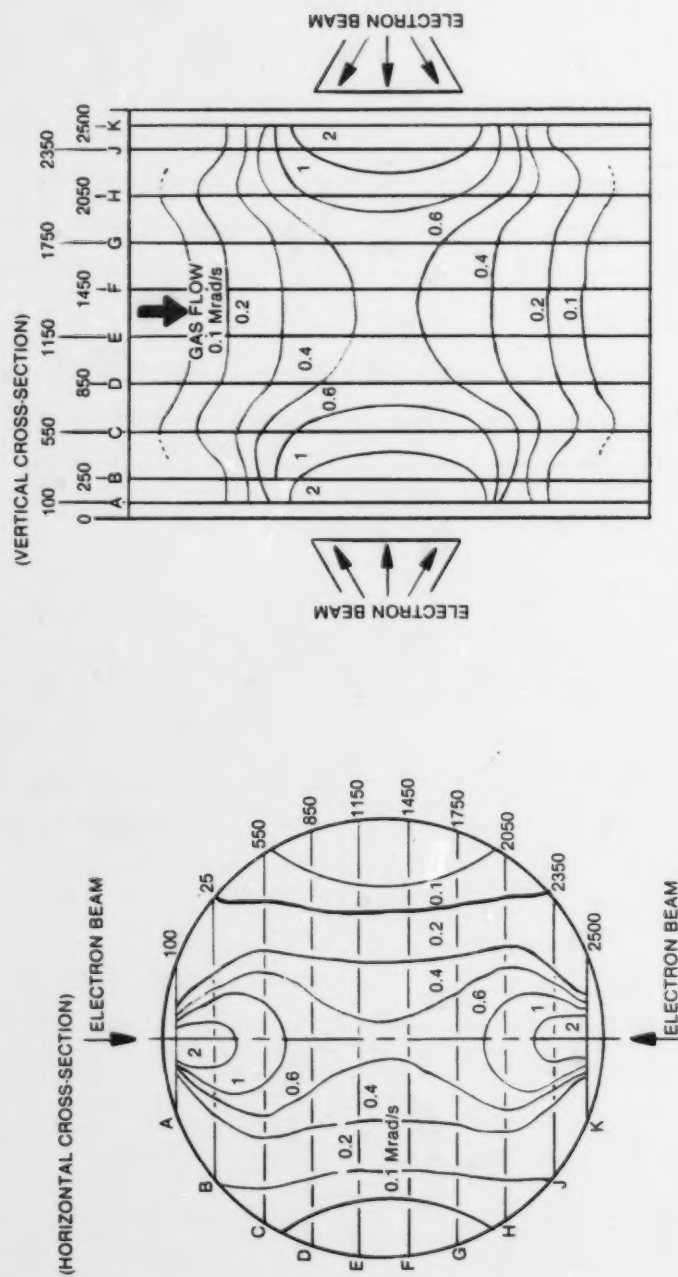
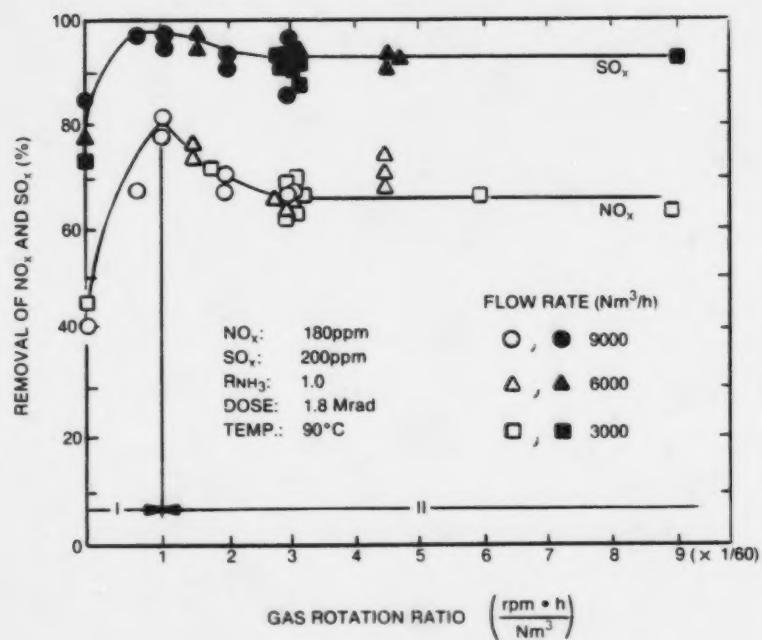


Figure 6-33 Dose Rate Distribution in Ebara Process Pilot Plant Reactor. \*

\* accelerating voltage = 600 kV.





$$\text{GAS ROTATION RATIO: } \frac{\text{REVOLUTIONS OF IMPELLER (rpm)}}{\text{GAS FLOW RATE (Nm}^3\text{/h)}}$$

Figure 6-34 Relationship Between Gas Rotation Ratio and SO<sub>x</sub> and NO<sub>x</sub> Removal Efficiencies.



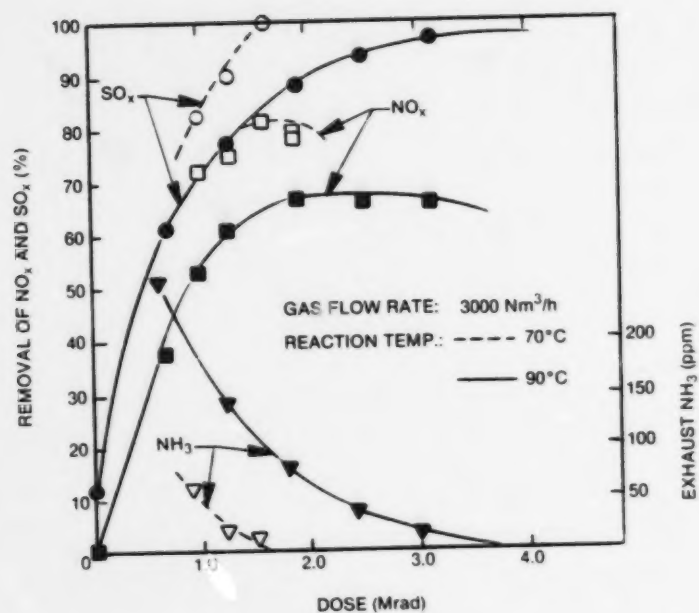


Figure 6-35 Effect of Dose on Removal Efficiencies and Exhaust NH<sub>3</sub>.\*

\* gas rotation ratio: 1/33.

Figure 6-35 were conducted at a gas rotation ratio of 1/33 units. Better results may be obtained with a ratio of 1/60.

Figure 6-36 shows the results of 600 hours of pilot plant operation at 1.5 Mrad and 90°C with a gas rotation ratio of 1/33. During this test period the pilot plant was shut down twice due to the shutdown of the the sintering machine. The inlet SO<sub>x</sub> concentration ranged from 180 to 250 ppm; the inlet NO<sub>x</sub> concentration was in the range of 170 to 210 ppm. The SO<sub>x</sub> and NO<sub>x</sub> removal efficiencies ranged from 92 to 97% and 75 to 85% , respectively, while unreacted NH<sub>3</sub> leakage at the reactor outlet ranged from 10 to 50 ppm. This high level of unreacted ammonia was caused by the frequent fluctuations in inlet SO<sub>x</sub> and NO<sub>x</sub> concentrations and by problems with the ammonia flow meter.

The balance of NO<sub>x</sub>, NH<sub>3</sub>, and SO<sub>x</sub> in three pilot plant test runs is shown in Table 6-18. Most of the NO<sub>x</sub>, NH<sub>3</sub>, and SO<sub>x</sub> were reacted and caught by the ESP, but a large portion of the NH<sub>3</sub> and SO<sub>x</sub> did deposit in the duct and a considerable amount of NO<sub>x</sub> was emitted from the recovery system. The total amounts of NH<sub>3</sub> and SO<sub>x</sub> were slightly larger than 100% presumably because of a sampling and analysis error. The NO<sub>x</sub> totals were considerably larger than 100%, which indicated that irradiation was causing the formation of NO<sub>x</sub> from N<sub>2</sub> and O<sub>2</sub>. Chemical analysis of the exhaust gas revealed the presence of N<sub>2</sub>O in concentrations ranging from 10 to 20 ppm.

TABLE 6-18. BALANCE OF NO<sub>x</sub>, NH<sub>3</sub> AND SO<sub>x</sub> (PERCENT OF INLET CONCENTRATION)

| Run No. | Component       | Caught by ESP | Deposit in Duct | Emitted | Total |
|---------|-----------------|---------------|-----------------|---------|-------|
| 1109    | NO <sub>x</sub> | 81            | 6               | 49      | 136   |
|         | NH <sub>3</sub> | 64            | 36              | 9       | 109   |
|         | SO <sub>x</sub> | 62            | 43              | 10      | 115   |
| 1111    | NO <sub>x</sub> | 87            | 6               | 31      | 124   |
|         | NH <sub>3</sub> | 65            | 36              | 10      | 111   |
|         | SO <sub>x</sub> | 64            | 40              | 8       | 112   |
| 1114    | NO <sub>x</sub> | 78            | 6               | 38      | 132   |
|         | NH <sub>3</sub> | 65            | 36              | 7       | 105   |
|         | SO <sub>x</sub> | 59            | 43              | 8       | 110   |

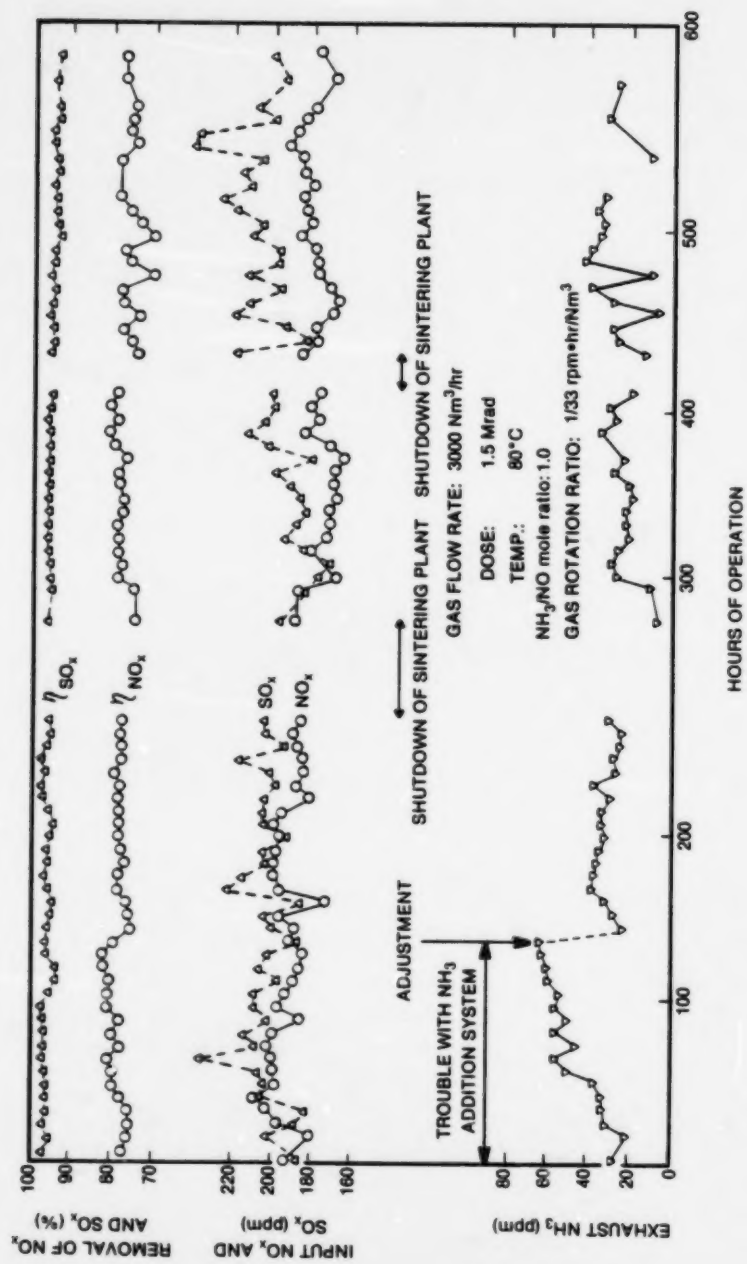


Figure 6-36 Results of 600 Hours of Continuous Ebara Process Pilot Plant Tests.

70A2873

During the test period, the titanium foil at the reactor window was often broken. Later, a foil with a titanium alloy was used which lasted for over two months. Ebara has developed a method of changing the foil without stopping the operation of the accelerator.

An X-ray diffraction analysis of products caught by the ESP indicated that the major compounds present were  $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ ,  $3\text{NH}_4\text{NO}_3 \cdot \text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ . Chemical analysis of a product obtained from a gas containing 220 ppm  $\text{SO}_2$  and 235 ppm  $\text{NO}_x$  with 700 ppm  $\text{NH}_3$  at  $90^\circ\text{C}$  revealed that the product contained 33.6%  $\text{SO}_4$ , 29.4%  $\text{NO}_3$ , 23.6%  $\text{NH}_3$ , and 0.9% C.

The results of a pilot plant test using  $\text{SO}_x$ - and  $\text{NO}_x$ -rich gas are shown in Figure 6-37 (13). About 80% of both  $\text{SO}_x$  and  $\text{NO}_x$  were removed at 1.8 Mrad with an ammonia stoichiometry of 1.0. With these conditions unreacted ammonia was about 50 ppm; the gas rotation ratio was poor (1/17) because of a limited ammonia supply and a flue gas volume of only 1,500  $\text{Nm}^3/\text{hr}$ . It is probable that about 90% of both  $\text{SO}_x$  and  $\text{NO}_x$  can be removed with a better rotation ratio, as shown in Figure 6-34.

For some of the tests, 0.1 - 0.5 g/ $\text{Nm}^3$  of fly ash (equivalent to 95-75% removal of fly ash from pulverized coal) were added to the system. The results indicated that the fly ash produced no adverse effect on the  $\text{SO}_x$  and  $\text{NO}_x$  removal efficiencies (13).

#### 6.6.3 Reaction Mechanism

Fundamental tests also were conducted on the reaction mechanism of the Ebara process. Although the reactions are complex, the major one appears to be the formation of oxidant radicals such as OH caused by the radiation of water vapor. In this reaction  $\text{SO}_2$  and NO are oxidized to form sulfuric acid and nitric acid mists; the mists react with ammonia to form fine crystals of sulfate and nitrate. Tests results also showed that the  $\text{SO}_2$  removal efficiency is slightly higher when the gas is cooled by a water spray rather than by a heat exchanger; the  $\text{NO}_x$  removal was not significantly different with the

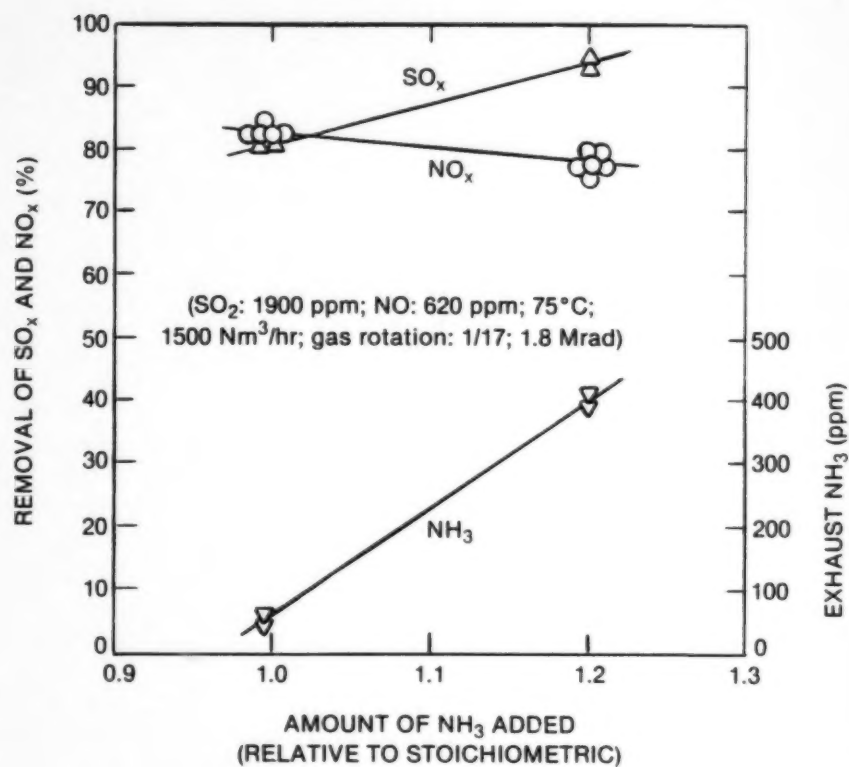


Figure 6-37 Removal of  $\text{SO}_x$  and  $\text{NO}_x$  vs. Amount of Ammonia Added.



two types of cooling. Presumably the fine water droplets in the spray combine with  $\text{SO}_2$  to form sulfuric acid mists which promote the formation of  $\text{SO}_3$  from  $\text{SO}_2$ .

#### 6.6.4 Ebara Process Commercial Plant Assumptions

Electron beam accelerators with capacities of 100 - 150 kW have been used commercially for various purposes without problems. A larger accelerator with a capacity of 500 kW will be commercialized in Japan in the near future. This 500 kW accelerator can treat 60,000 to 70,000  $\text{Nm}^3/\text{hr}$  of flue gas. Since it is advantageous to use at least 2 accelerators with a reactor, an economical minimum capacity for a reactor may be 120,000 to 140,000  $\text{Nm}^3/\text{hr}$ , which is equivalent to 35 to 50 MW.

Figure 6-38 shows a layout plan for a commercial Ebara process plant with a capacity of treating 1,000,000  $\text{Nm}^3/\text{hr}$  of flue gas from a utility boiler (290 MW for coal and 350 MW for oil). The flue gas contains 60 ppm  $\text{NO}_x$ , 1,000 ppm  $\text{SO}_x$ , and 100  $\text{mg}/\text{Nm}^3$  of dust. In such a plant the  $150^\circ\text{C}$  flue gas is cooled by a heat exchanger to about  $110^\circ\text{C}$  and then indirectly cooled to  $70^\circ\text{C}$  with water tubes. The cooled gas is mixed with ammonia and treated by two reactors in parallel (diameter approximately 4 m), and sent through an ESP.

A total of 14-16 accelerators (500 kW each) may be used to remove 80% of  $\text{NO}_x$  and 90% of  $\text{SO}_x$ . The treated gas will probably contain 120 ppm  $\text{NO}_x$ , and 100 ppm  $\text{SO}_x$ , and less than 20 ppm unreacted  $\text{NH}_3$  with about 15  $\text{mg}/\text{Nm}^3$  of dust.

Ebara estimated the investment cost of the electron beam process to be close to that of a conventional wet FGD system, provided that a large accelerator (500 kW) is available at a reasonable cost. The estimated utility requirements for the 1,000,000  $\text{Nm}^3/\text{hr}$  plant are shown in Table 6-19. The electron beam system's total power consumption of 10,000 kWhr accounts for 2.9 to 3.4% of the power generated by the power plant. This power consumption is



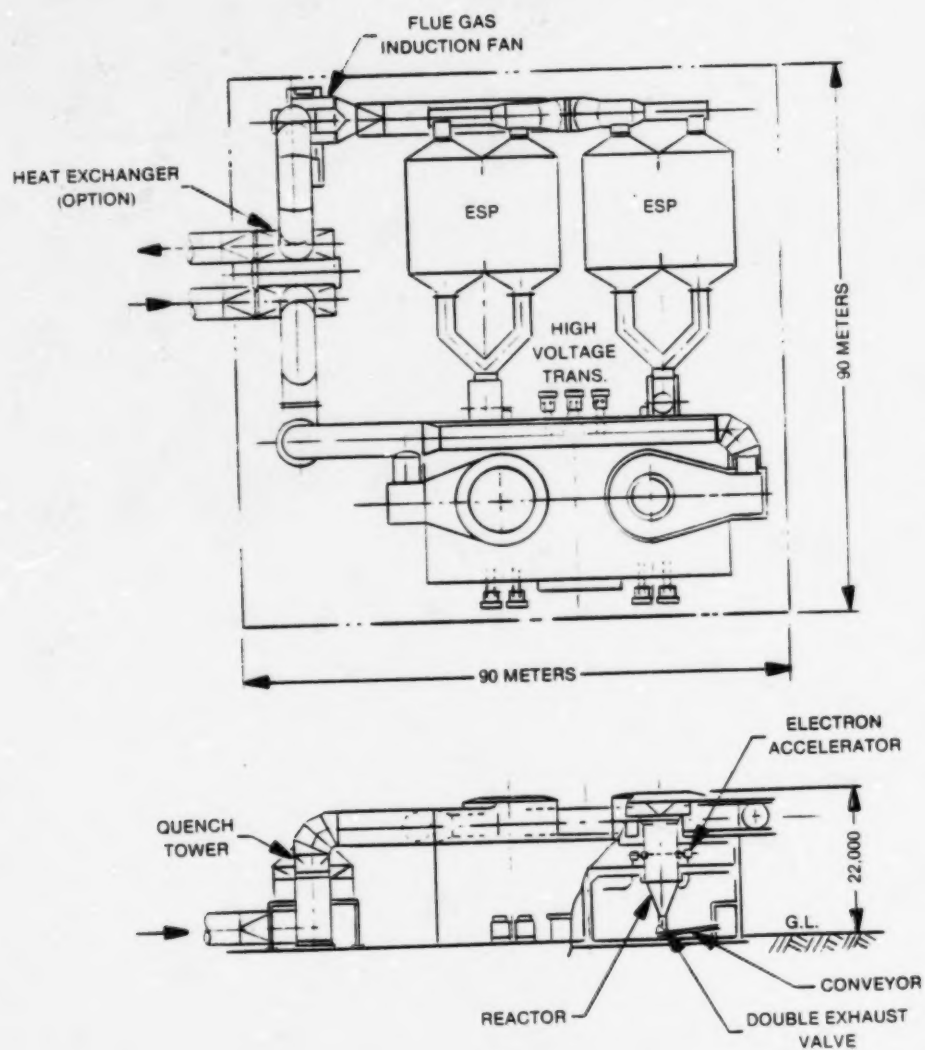


Figure 6-38 Layout Plan for a 1,000,000 Nm<sup>3</sup>/hr Commercial Ebara Process Plant.

TABLE 6-19. ESTIMATED UTILITY REQUIREMENTS PER HOUR ESTIMATED FOR EBARA PROCESS SYSTEM APPLIED TO A UTILITY BOILER  
(FLUE GAS 1,000,000 Nm<sup>3</sup>/hr, 350 MW FOR OIL, 290 MW FOR COAL)

|         |                               |             |
|---------|-------------------------------|-------------|
| Power   | Electron beam accelerator     | 6,900 kWhr  |
|         | Other                         | 3,100 kWhr  |
|         | Total                         | 10,000 kWhr |
| Steam   | Ammonia vaporization          | 1 ton       |
|         | Soot blowing                  | 1 ton       |
|         | Total                         | 2 ton       |
| Water   | Gas cooling                   | 33 ton      |
|         | Other                         | 1 ton       |
|         | Total                         | 34 ton      |
| Ammonia | 0.94 of stoichiometric amount | 2 ton       |

TABLE 6-20. COST COMPARISON OF FLUE GAS TREATMENT PROCESSES (500 MWe) (13)  
(Cost estimates established by Gibbs & Hill, Inc., New York. SO<sub>2</sub> = 1900 ppm, 90% removed; NO<sub>x</sub> = 620 ppm, 90% removed; lime scrubber does not remove NO<sub>x</sub>.)

|                                        | Avco/Ebara         | Lime Scrubber    |
|----------------------------------------|--------------------|------------------|
| Total capital cost \$M                 | 43                 | 60               |
| \$/kW                                  | 86                 | 120              |
|                                        | (\$/MWh)           | (\$/MWh)         |
| Depreciation and overhead <sup>a</sup> | 2.4                | 3.4              |
| Variable operating cost <sup>b</sup>   | 2.5                | 2.8              |
| Reheat cost                            | 0                  | 1.0              |
| Total operating cost                   | 4.9                | 7.2              |
| Byproduct charge/(credit)              | (0.6) <sup>c</sup> | 0.4 <sup>d</sup> |
| Net operating cost                     | 4.3                | 7.6              |
| Total first year cost                  | \$14M              | \$26M            |

<sup>a</sup> 80% load factor; annual cost = 20% of total capital.

<sup>b</sup> Ammonia at \$130/ton.

<sup>c</sup> Sold as agricultural fertilizer at \$15/ton.

<sup>d</sup> Does not include cost of disposal site and preparation.

slightly more than to that of a combination of SCR and wet FGD. SCR requires about 0.2% and FGD consumes 2 to 2.5% (excluding gas reheating) of the total power generated by the plant.

In Table 6-20 estimated costs for the AVCO/Ebara process are compared with the costs of lime scrubbing. The cost of the AVCO/Ebara process assumes the use of simple water spraying for gas cooling and is considerably lower than the cost of lime scrubbing.

#### 6.6.5 Evaluation

The Ebara/AVCO electron beam irradiation process is unique and has the following advantages:

- (1)  $\text{SO}_x$  and  $\text{NO}_x$  are removed simultaneously.
- (2) Since it is a dry process, wastewater treatment is not necessary.
- (3) Ammonia,  $\text{SO}_x$  and  $\text{NO}_x$  are recovered as useful byproducts.
- (4) The process is simple; the only problem so far has been the need for occasional renewal of the foil at the accelerator window.

However, the process does have the following disadvantages:

- (1) For treating flue gas from coal, a dust removal facility is needed upstream of the reactor in order to obtain a useful byproduct.
- (2) Gas cooling to about  $70^\circ\text{C}$  is needed to obtain a high  $\text{NO}_x/\text{SO}_x$  removal efficiency.
- (3) Large amounts of  $\text{NH}_3$  and  $\text{N}_2\text{O}$  may be emitted for high removal efficiencies from  $\text{SO}_x$ -rich gas.

Fly ash from coal has been used as fertilizer to supply micronutrients such as zinc and boron to certain soils. For this reason small amounts of fly ash in the Ebara process byproduct ammonium may be acceptable but large amounts decrease the compounds' fertilizer value.

Using a water spray for cooling is simpler and produces a higher  $\text{SO}_2$  removal efficiency than indirect cooling. The gas can be cooled to  $70^\circ\text{C}$  without producing any wastewater. Unfortunately water spraying may cause the ammonium compounds to absorb moisture when a large amount of spray is used and the moisture content of the gas also exceeds the critical humidity for the compounds.

The amount of unreacted ammonia from the Ebara reactor may be reduced with improved control of ammonia addition. This can be achieved by measuring the concentration of outlet  $\text{NH}_3$  as well as that of inlet  $\text{SO}_x$  and  $\text{NO}_x$ . The formation of  $\text{N}_2\text{O}$  may be also reduced, but cannot be prevented. A substantial concentration of  $\text{N}_2\text{O}$  occurs naturally, so the emission of a small additional amount will not produce any adverse environmental effect. Nonetheless, further study is necessary to determine ways of reducing  $\text{N}_2\text{O}$  formation.

Table 6-18 shows that a considerable portion of the byproducts deposited in the system ductwork. This deposition may be eliminated by increasing the gas velocity through the duct.

Although there are many simultaneous  $\text{SO}_x/\text{NO}_x$  removal processes, the Ebara process is the only one that may be commercially applicable for byproduct recovery of  $\text{SO}_x$ ,  $\text{NO}_x$ , and  $\text{NH}_3$ . Additional tests using a larger pilot plant with gases of various compositions will be necessary for definite proof of this commercial potential.

## 6.7 MKK POTASSIUM-EDTA WET SIMULTANEOUS SO<sub>x</sub>/NO<sub>x</sub> REMOVAL PROCESS

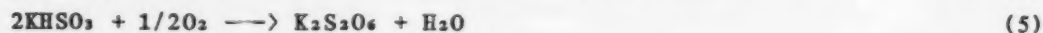
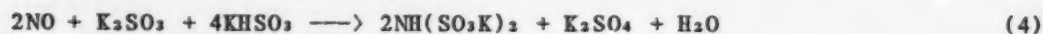
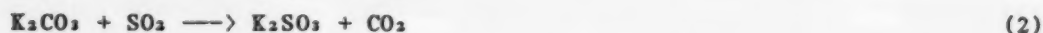
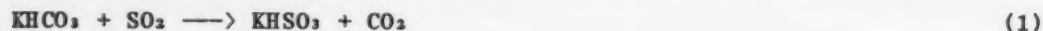
### 6.7.1 Introduction

The potassium-EDTA wet process simultaneously removes SO<sub>x</sub> and NO<sub>x</sub> from flue gas by using a solution containing potassium salts, ferrous sulfate, and EDTA (ethylenediamine tetraacetic acid). NO<sub>x</sub> is converted to N<sub>2</sub> and SO<sub>x</sub> to elemental sulfur. The process was developed by Mr. Y. Kobayashi who was associated with Mitsubishi Kakoki Kaisha (MKK) and is now with Hitachi Zosen (HZ). The process resembles the Kureha KDSN process which also uses potassium salts, ferrous sulfate, and EDTA to convert SO<sub>x</sub> to elemental sulfur(4). Each process has been studied independently.

The MKK process is a combination of several commercially proven steps plus a few new steps; bench scale tests have been conducted on the new steps.

### 6.7.2 Process Description

Figure 6-39 presents a flowsheet of the MKK process. Flue gas is sent into an absorber and treated with a solution containing KHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, FeSO<sub>4</sub>, and EDTA. About 99% of SO<sub>x</sub> and 90% of NO<sub>x</sub> can be absorbed by the following reactions:



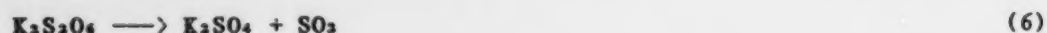
EDTA and FeSO<sub>4</sub> promote the absorption of NO by reaction (4) to form potassium imidodisulfonate (NH(SO<sub>3</sub>K)<sub>2</sub>). K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>6</sub> and NH(SO<sub>3</sub>K)<sub>2</sub> are crystallized in the liquor, separated by a thickener and filter, and then heated in a two-stage flash dryer. The heater uses hot gas obtained by incineration of a portion of the H<sub>2</sub>S that was produced by the reduction of the



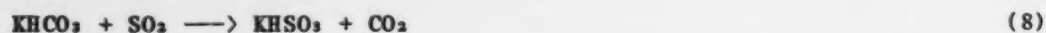
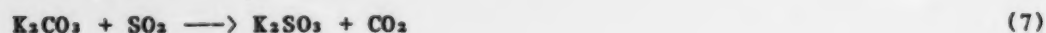




potassium salts. The first stage of heating is for drying. During the second stage at 370°C,  $K_2S_2O_6$  is decomposed to  $K_2SO_4$  and  $SO_2$ :

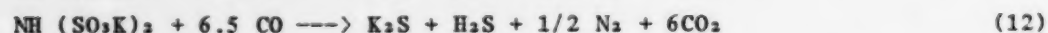
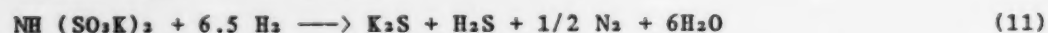
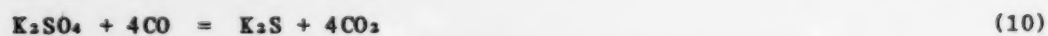
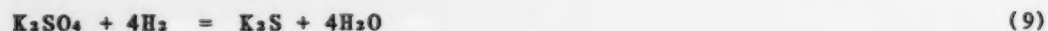


The  $SO_2$  contained in the hot gas, as well as that released from the  $K_2S_2O_6$ , is absorbed by a solution containing  $K_2CO_3$  and  $KHCO_3$  (obtained by the carbonation of  $K_2S$ ).

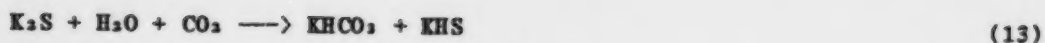


The liquor leaving the  $SO_2$  absorber contains  $KHCO_3$ ,  $K_2CO_3$  and  $KHSO_3$  and is mixed with EDTA, KOH, and  $FeSO_4$ , and sent into the main absorber. In the main absorber  $SO_x$  and  $NO_x$  are removed simultaneously by the 50-60°C liquor (pH 6.8-7.0). A large  $(SO_2 + HSO_3)/NO$  ratio is needed in order to attain a high NO removal efficiency. Incineration of a portion of the recovered  $H_2S$  increases both the ratio and the NO removal efficiency.

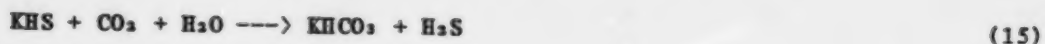
The drying process produces a solid consisting of  $K_2SO_4$  and  $NH(SO_3K)_2$ . The solid is caught by a cyclone, jet milled into a very fine powder of about 5 $\mu$ m, and then sent into a reduction furnace. In the furnace a 1,400-1,500°C hot gas instantaneously reduces the powder to  $K_2S$  at 800-900°C. The reducing gas is produced by the partial oxidation of fuel oil by oxygen and steam:



$K_2S$  is dissolved in water and the solution is sent to the No. 1 carbonation tower where it is treated with  $CO_2$  at 80-90°C (pH 9.5-12.5):



The resulting solution is carbonated at 40–60°C (pH of 8–9.5) in the No.2 tower:



In actual practice, 3 to 4 towers in series may be needed to attain a high carbonation efficiency.

As it leaves the tower, the liquor contains  $\text{K}_2\text{CO}_3$  and  $\text{KHCO}_3$ . Next it is sent into the  $\text{SO}_2$  absorber; the gas (containing  $\text{H}_2\text{S}$  and  $\text{CO}_2$ ) leaving the tower is sent into an  $\text{H}_2\text{S}$  absorber, where  $\text{H}_2\text{S}$  is selectively absorbed by an amine solution at 40°C.

The gas which leaves the  $\text{H}_2\text{S}$  absorber containing  $\text{CO}_2$  is returned to the No. 2 tower. The liquor leaving the  $\text{H}_2\text{S}$  absorber is sent to the  $\text{H}_2\text{S}$  stripper, where steam is injected to vaporize  $\text{H}_2\text{S}$ . Most of the  $\text{H}_2\text{S}$  is sent to a Claus furnace where elemental sulfur is recovered and a portion of  $\text{H}_2\text{S}$  is incinerated. This produces a hot gas for the heating process. The amount of  $\text{H}_2\text{S}$  incinerated is adjusted according to the inlet  $\text{O}_2$ ,  $\text{SO}_2$ , and  $\text{NO}_x$  concentrations and the required  $\text{NO}_x$  removal efficiency.

### 6.7.3 Requirements and Costs

Table 6-21 shows the amounts and costs of the estimated raw materials and utilities needed for an MKK system designed to treat 150°C flue gas from a 1,000 MW coal-fired boiler containing 4.5%  $\text{O}_2$ , 900 ppm  $\text{SO}_x$ , 300 ppm  $\text{NO}_x$ , 50 ppm  $\text{HCl}$ , and 100 mg/ $\text{Nm}^3$  of fly ash. The system will remove 99% of  $\text{SO}_x$  and 80% of  $\text{NO}_x$ .

TABLE 6-21. UTILITY AND MATERIAL REQUIREMENTS AND COSTS OF AN MKK PROCESS SYSTEM FOR A MW COAL-FIRED BOILER (1980) (For 1000 MW hr)

|                              | Consumption          | Unit Cost           | Cost (1000 Yen) |
|------------------------------|----------------------|---------------------|-----------------|
| EDTA                         | 282.9 kg             | 600 yen/kg          | 149.7           |
| FeSO <sub>4</sub>            | 320 g                | 5 yen/kg            | 1.6             |
| KOH                          | 188 kg               | 150 yen/kg          | 29.0            |
| High S oil (asphalt)         | 8690 l               | 50 yen/l            | 434.5           |
| Low S oil                    | 3450 l               | 57 yen/l            | 196.6           |
| O <sub>2</sub> (95%)         | 6400 Nm <sup>3</sup> | yen/Nm <sup>3</sup> | 75.5            |
| Power                        | 29100 Kwhr           | 9 yen/Kwhr          | 261.9           |
| Industrial Water             | 170 t                | 10 yen/t            | 1.7             |
| Cooling water<br>(sea water) | 1250 t               | 2 yen/t             | 2.5             |
| Others                       |                      |                     | 8.0             |
| TOTAL                        |                      |                     | 1160.1          |
| Recovered S                  | 4280 kg              | 22 yen/kg           | 94.2            |

It is estimated that such a system produces 700 kg/hr of sludge containing fly ash as well as 2,030 kg/hr of wastewater. The wastewater is needed to prevent the accumulation of chlorine in the system.

The investment cost is estimated at 18.8 billion yen or 18,800 yen/kW. The annual cost for 7,000 hours full load operation is shown in Table 6-22.

The relationship between the annualized treatment cost and the inlet O<sub>2</sub> percentage, NO<sub>x</sub> concentrations and NO<sub>x</sub> removal efficiency is shown in Figure 6-40. The treatment cost increases sharply with an increase in the inlet concentrations and the removal ratio. An increase in the inlet SO<sub>2</sub> concentration, unlike a similar increase in the inlet NO<sub>x</sub> concentration, does not have a significant effect on the cost. Over 99% of SO<sub>2</sub> is absorbed, even with 75% NO<sub>x</sub> removal. Although an increase in SO<sub>2</sub> necessitates the treatment of a larger amount of potassium salts during the reduction and carbonation steps, a high SO<sub>2</sub>/NO<sub>x</sub> ratio favors NO<sub>x</sub> removal and reduces the amount of H<sub>2</sub>S needed to produce SO<sub>2</sub>. It is also estimated that when the HCl concentration increases by 10 ppm, the cost subsequently increases by 0.037 yen/kWhr due to the larger amount of wastewater which must be treated.

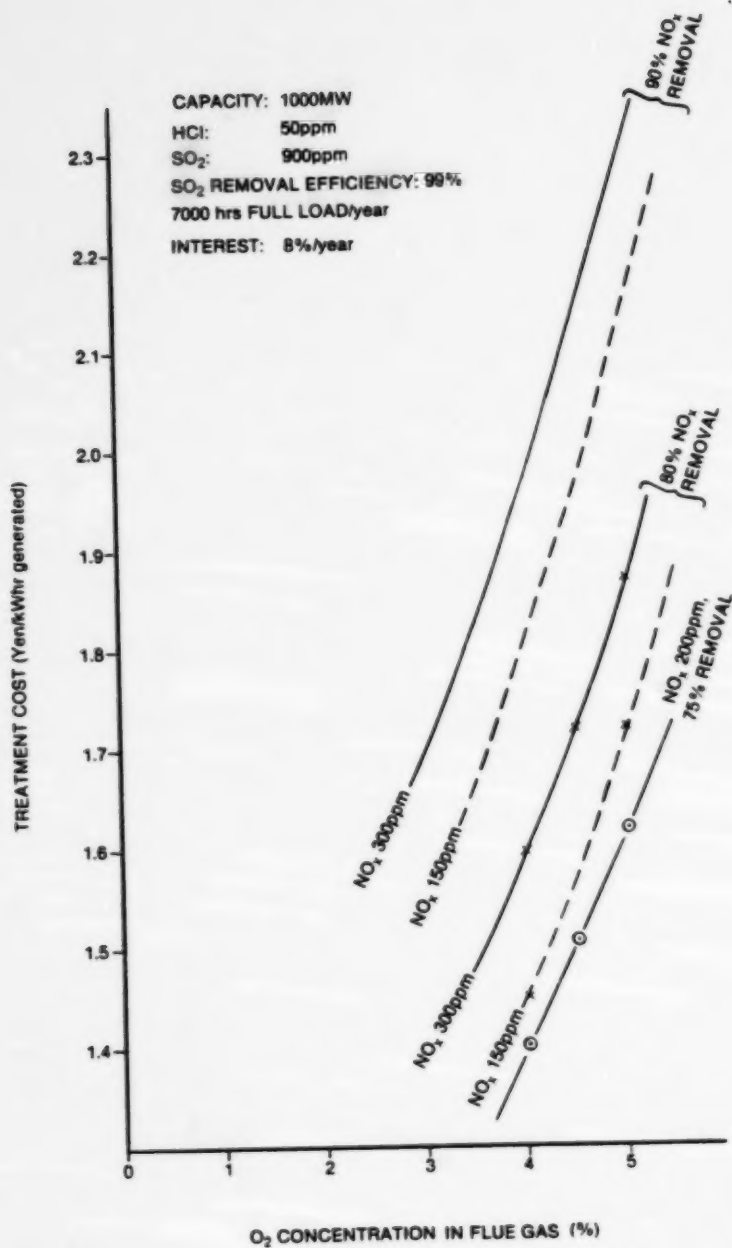


Figure 6-40 Annualized Cost for Various Operating Conditions in an MKK Process System.

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TABLE 6-22. ANNUAL COST OF AN MKK PROCESS SYSTEM  
FOR A 1000 MW COAL-FIRED BOILER

| Item             | Calculation Basis                         | Cost (10 <sup>6</sup> yen) |
|------------------|-------------------------------------------|----------------------------|
| (1) Capital Cost |                                           |                            |
| Depreciation     | Investment Cost $\times 0.9 \times (1/7)$ | 2,417.1                    |
| Interest         | " $\times 0.08 \times 0.55$               | 827.2                      |
| Tax              | " $\times 0.014 \times 0.55$              | 144.8                      |
| Insurance        | " $\times 0.4 \times 0.003$               | 22.6                       |
| Total            |                                           | 3,411.7                    |
| (2) Direct Cost  |                                           |                            |
| Labor            | 8,000 $\times$ 24 (person)                | 192.0                      |
| Maintenance      | Investment cost $\times 0.015$            | 282.0                      |
| (3) Chemicals    |                                           |                            |
| Utilities        | 1,116,100 $\times$ 7000                   | 8,120.7                    |
| (4) Related cost | (2) + (3) $\times 0.08$                   | 687.6                      |
| (5) Total        | (1) + (2) + (3) + (4)                     | 12,694.0                   |
| (6) By-product S | 94,200 $\times$ 7,000                     | 659.4                      |
| (7) Difference   |                                           | 12,034.5                   |
| ANNUALIZED COST  | (7) 7,000,000,000 (kWhr)                  | 1.719 yen/kWhr             |

#### 6.7.4 Evaluation

The MKK system is a combination of several steps most of which have been proven to be feasible through commercial operation or pilot plant tests. One exception is the step in which  $K_2SO_4$  and  $NH(SO_3K)_2$  are instantaneously reduced to  $K_2S$ . Basic chemical and thermodynamic studies related to the process have been conducted, although the total system has not been tested yet at a pilot plant.

One advantage that potassium scrubbing has over sodium scrubbing is that  $K_2SO_4$ ,  $NH(SO_3K)_2$ , and  $K_2S_2O_8$  are less soluble than the corresponding sodium salts, and can be separated from the mother liquor. On the other hand, for carbonation of  $K_2S$ , a larger  $CO_2/H_2S$  ratio is needed than for  $Na_2S$ , because  $KHCO_3$  is more soluble than  $NaHCO_3$  and cannot be crystallized out.



The use of oxygen instead of air in the MKK system substantially reduces fuel consumption, gas volume, and reactor size. Moreover, the loss of  $\text{CO}_2$  is eliminated because it is not necessary to purge  $\text{N}_2$  as it is when air is used. Thus, the overall cost may be reduced by using oxygen.

Simultaneous  $\text{SO}_x$  and  $\text{NO}_x$  removal and the conversion of  $\text{SO}_x$  to elemental sulfur are other advantages of the MKK process. However, the process does require complex equipment including an oxygen generator, Claus furnace, and wastewater treatment system in addition to the facilities shown in Figure 6-39. Pilot plant tests on the reduction and carbonation steps are needed to prove the feasibility of the process. Although the wastewater treatment system appears to be complex, it may not prove to be a serious problem because of the small quantity of wastewater produced.

The system has a silo for solids storage and a storage tank for the absorbing liquor. This allows the continuous operation of the absorber and reduction furnace even when other steps in the process must shut down.

The estimated investment and operation costs for an MKK system are slightly lower than those for a combined SCR/FGD system. For more accurate cost estimates, a pilot plant test of the entire system is necessary. Since 90%  $\text{NO}_x$  removal requires a large multi-stage absorber and a large pressure drop, 80% removal may be more practical. Because its cost increases sharply with increases in the inlet  $\text{O}_2$  and  $\text{NO}_x$  concentrations, the MKK process may be best suited to flue gas from high-sulfur oil rather than from coal. An increase in the  $\text{SO}_2$  content of flue gas does not significantly increase the operation cost since it aids in  $\text{NO}_x$  removal.

The MKK process, as well as the Kureha KDSN process, is sophisticated and probably will not be used commercially in the near future. The ability of both of these processes to byproduce elemental sulfur and to remove  $\text{NO}_x$  without using ammonia is an attractive feature. This type of  $\text{NO}_x/\text{SO}_x$  removal technology should be further studied as a possible alternative to the SCR/FGD combination. The latter may experience problems when widely used, due



to its ammonia consumption and the difficulty associated with disposal of its byproduct sulfur compounds.

## 6.8 NO OXIDATION CATALYST

### 6.8.1 Introduction

Almost all of the  $\text{NO}_x$  in combustion gases is present in the form of NO. NO is only slightly absorbed in most solutions except for those which contain a complexing agent such as EDTA with ferrous ion.  $\text{NO}_2$ , on the other hand, is readily absorbed in solutions. The equimolecular mixture of  $\text{NO}_2$  and NO is also fairly well absorbed. In several wet  $\text{NO}_x$  removal processes, most of the NO is first oxidized to  $\text{NO}_2$  using chemicals such as ozone or chlorine dioxide. However, these chemicals are expensive or cause wastewater treatment problems.

In the air NO is oxidized slowly to  $\text{NO}_2$ . As the temperature increases this reaction rate also increases, but a high temperature lowers the NO conversion ratio in equilibrium. The theoretical NO/ $\text{NO}_2$  conversion ratio in air is about 80% at 300°C and 20% at 500°C. Catalytic oxidation of NO at a relatively low temperature may cause the conversion of a considerable portion of NO in a short time period.

### 6.8.2 Catalytic Oxidation Tests

In Japan, H. Tominaga has conducted extensive studies of catalytic oxidation of NO to  $\text{NO}_2$  (13). Tominagas' preliminary tests indicate that zeolite impregnated with heavy metals is effective as a catalyst. He used synthetic zeolite (molecular sieve) 13X and 13Y after the Na ion was exchanged with heavy metal ions. Heavy metal compounds of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  were used for the ion exchange. The exchange ratio was 67% with Cu (II), 44% with Cr (III), 74% with Co (II), and 47% with Ni (II).

A pyrex glass tube (13 mm inner diameter and 500 mm long) was used for the fixed bed reactor. Mixtures of NO and O<sub>2</sub>, diluted with He, were passed through the reactor after being preheated. In some of the tests, the effects of adding H<sub>2</sub>O and SO<sub>2</sub> to the gas were studied. Two grams of catalyst between 10 mesh and 40 mesh were used for an SV of 30,000 hr<sup>-1</sup>, four grams for an SV of 15,000 hr<sup>-1</sup>. Results of tests using 13x catalysts are shown in Figure 6-41.

It is interesting to note that in some of the tests with the Cr (III) catalyst the conversion ratio exceeded 70% (above the theoretical value) at 400°C in the presence of water vapor.

#### 6.8.3 Evaluation

At 400°C or below, the catalysts tested by Tominaga are poisoned by SO<sub>2</sub>. Although the poisoning is not noticeable at 450°C, the conversion ratio at this temperature may be too low to be useful. For this reason, the process does not seem to be applicable to SO<sub>2</sub>-rich gas.

The process may work well for gases which do not contain SO<sub>x</sub>. With these gases it can be used to convert about 50% of NO to NO<sub>2</sub> at 350°-400°C, in order to achieve equimolecular absorption.

### 6.9 OTHER PROCESSES AND PLANTS

#### 6.9.1 Copper Oxide Process for Simultaneous NO<sub>x</sub>/SO<sub>x</sub> Removal (Shell Process)

In 1973, Showa Yokkaichi Sekiyu Co. (SYS) installed at its Yokkaichi Refinery, a Shell Process FGD unit which uses copper oxide as the acceptor. In the process, SO<sub>x</sub> absorption forms copper sulfate, which is treated with hydrogen to regenerate Cu and concentrated SO<sub>2</sub> gas. The latter is sent to a Claus furnace for production of elemental sulfur.

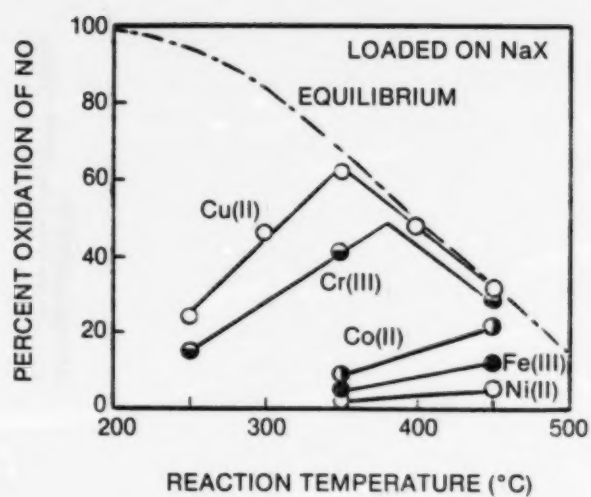


Figure 6-41 Oxidation Ratio vs. Catalyst Type and Temperature.

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Since copper sulfate is a catalyst for SCR of  $\text{NO}_x$ , ammonia has been added to flue gas since 1975 to remove about 40% of  $\text{NO}_x$  and about 90% of  $\text{SO}_x$  to meet the local regulation(1). The operability of the unit, however, has been low except that for one year of continuous operation in 1978. SYS does not plan to install a new unit.

#### 6.9.2 Activated Coke Simultaneous Removal (Mitsui Mining Process)

Mitsui Mining Company has developed a simultaneous  $\text{SO}_x/\text{NO}_x$  removal process which uses activated coke produced by a special coal treatment. A pilot plant with a capacity of treating 1,000  $\text{Nm}^3/\text{hr}$  of flue gas from an oil-fired boilers at  $150^\circ\text{C}$  has been operated to remove over 80% of the  $\text{NO}_x$  and about 98% of the  $\text{SO}_2$ . Coal fly ash was added to the flue gas to study the effect of the ash. The pilot plant has two reactors in series; most of the  $\text{SO}_2$  is absorbed in the first reactor by the coke. A small portion of ammonia is fed to the first reactor, but the major portion is fed to the second reactor where most of the  $\text{NO}_x$  is converted to  $\text{N}_2$  and  $\text{H}_2\text{O}$  by reacting with the ammonia.  $\text{SO}_2$  is further adsorbed in the second reactor.

The adsorbed  $\text{SO}_2$  is regenerated by a hot gas. The recovered concentrated  $\text{SO}_2$  may be used for sulfuric acid or liquid  $\text{SO}_2$  production. Mitsui Mining has conducted some studies on a method of producing elemental sulfur from the  $\text{SO}_2$ .

#### 6.9.3 Molecular Sieve Process for $\text{NO}$ Adsorption

Nissan Chemical Industries installed an  $\text{NO}_x$  recovery plant which uses a molecular sieve produced by Union Carbide Corp. USA, to treat 22,000  $\text{Nm}^3/\text{hr}$  of tail gas from a nitric acid plant. The plant reduces the  $\text{NO}_x$  concentration in gas from 1,000 ppm to 50 ppm (1). The adsorbed  $\text{NO}_x$  eventually is thermally desorbed and returned to the nitric acid plant. The plant was commissioned in 1976 and has operated successfully for over five years without requiring any replacement of the original molecular sieve.

#### 6.9.4 Sumitomo-Fujikasui Wet Simultaneous Removal Process

Sumitomo Metal and Fujikasui Engineering have developed a wet simultaneous removal process which uses  $\text{ClO}_2$  as the oxidizing agent and  $\text{NaOH}$  as the absorbent. In 1973 and 1974 they constructed three medium-sized commercial plants, as shown in Table 6-2. The process can remove about 90% of both  $\text{SO}_x$  and  $\text{NO}_x$  but may not be suitable for large plants, because a large amount of  $\text{NaOH}$  is consumed and the waste liquor containing sodium chloride, nitrate, and sulfate must be treated (1).

Sumitomo and Fujikasui have also developed a modified process which uses  $\text{ClO}_2$  as the oxidizing agent and  $\text{CaCO}_3$  slurry containing a catalyst as the absorbent. In 1976 they built a demonstration plant which can treat 25,000  $\text{Nm}^3/\text{hr}$  of flue gas from an iron ore sintering machine. The modified process is less costly than the sodium process but still produces waste liquor containing calcium chloride and nitrate which requires treatment (1). There has been no further development of either of the processes.

#### 6.9.5 In-Furnace $\text{NO}_x$ Removal (Three Stage Combustion - Hitachi Zosen) (15)

Hitachi Zosen has conducted tests of in-furnace  $\text{NO}_x$  removal, a process they call "three stage combustion". The process is similar to the MACT process described in Section 6.4. Figure 6-42 shows a horizontal cylindrical test furnace with a length of 7m and an inner diameter of 1.5m. The furnace has a capacity of burning 200 kg/hr of pulverized coal. Some of the three stage combustion test results are shown in Figure 6-43. The  $\text{NO}_x$  concentration was about 800 ppm with a conventional burner, 600 ppm with a staged-combustion burner, and about 100 ppm when 30% of the coal was injected as the secondary fuel, with air introduced for complete combustion. In all of the tests, the CO in the flue gas was below 100 ppm and the amount of combustible components in the fly ash was less than 5%.

Hitachi Zosen plans to conduct additional tests using a larger furnace which can burn 2,000 kg/hr of pulverized coal.



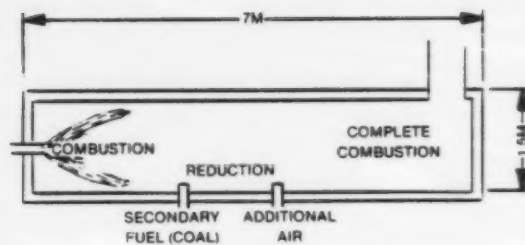


Figure 6-42 Hitachi Zosen's Three Stage Combustion Test Furnace.

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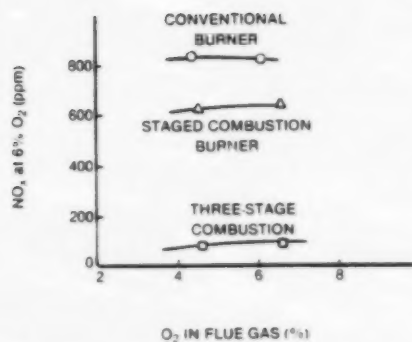


Figure 6-43 Results of Three Stage Combustion Tests. (in-furnace combustion)

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